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Atomic Systems With a Closed Core Plus Two Electrons.

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ATOMIC SYSTEMS WITH A CLOSED CORE PLUS TWO ELECTRONS

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TO FEFE AND OUR CHILDREN

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ABSTRACT

This dissertation is divided into two parts. Part I consists of the formulation of a simplified method of superposition of configurations of Weiss for the calculation of detachment potentials for systems with two electrons outside a closed core. The simplification does not impair the accuracy of the results. For the detachment of potentials of Be, Li^- and Na^- all agree with Weiss to within 0.01 eV. It has the further advantage of the ease of constructing projection operators used in determining autoionization states for e^--alkali atom systems, similar to the method proposed by Hahn, O'Malley and Spruch. For Li three autoionization states have been found below the $1s^2 3s$ level and four below the $1s^2 3p$ level. Only one autoionization state is found for Na.

Part II deals with an optical potential method for the calculation of the elastic scattering of positron from hydrogen atom. The single-particle states of the electron are chosen to be the hydrogenic solutions while the positron states are obtained by using a model polarization potential. Various models are investigated and a choice is made which effectively maximizes the calculated phase shifts through second-order in the perturbation expansion of the optical potential. Phase shifts thus obtained yield approximately 67%-80% of the difference between the static Hartree results and the variational

results of Schwartz.

PART I

MULTICONFIGURATION HARTREE-FOCK DESCRIPTION OF SYSTEMS WITH A CLOSED CORE PLUS TWO ELECTRONS

I-1. INTRODUCTION

The electron affinity (EA) of atoms is of interest to both physicists and chemists.[1] For the case of alkali atoms the EA can generally be computed more accurately than can be determined experimentally. Nonetheless such calculations are difficult because the EA is the small difference between two comparatively large numbers, the atom energy E_o and the ion energy E_-. An accurate direct calculation of the EA can only be obtained if E_o and E_- are computed with a high degree of precision or if E_o and E_- are known to be computed with the same absolute error.

Because of the computational difficulty involved in obtaining accurate values for the total energy of systems of more than two electrons, extrapolation procedures have been developed which utilize precise experimental values for the total energy of atoms and positive ions in the isoelectronic sequence. The first class of approximations fits the experimentally determined ionization potentials of the isoelectronic sequence to an analytic function of Z, the nuclear charge, and extrapolates to find the detachment potential of the lowest member of the sequence.[2-5]

Glockler[2] was the first to use an extrapolation formula to calculate the ionization potential (IP). He suggested, in 1934, the simple parabolic relation of $IP(Z) = (aZ^2 - bZ + c)/n^2$, in which a, b, c, and n are parameters to be obtained from experimental values of

TABLE I: GLOCKLER'S EXTRAPOLATION FORMULA

Shell	Number of Electrons	a	b	c	a/n^2
K	1	13.54	-	-	13.54
	2	13.54	16.87	4.06	
L	3	3.43	11.25	8.25	3.39
	4	3.43	15.10	14.77	

$$IP(Z) = (aZ^2 - bZ + c)/n^2 \text{ (eV)}$$

Sample calculations:

$EA(H) = (13.54 \times 1^2 - 16.87 \times 1 + 4.06)/1 = 0.73$ eV.

$IP(He) = (13.54 \times 2^2 - 16.87 \times 2 + 4.06)/1 = 24.48$ eV.

$EA(Li) = (3.43 \times 3^2 - 15.10 \times 3 + 14.77)$
$\times 3.39/3.43 = 0.34$ eV.

$IP(Be) = (3.43 \times 4^2 - 15.10 \times 4 + 14.77)$
$\times 3.39/3.43 = 9.25$ eV.

members of the iso-electronic sequence. Table I gives the values of the parameters obtained from experimental data available to him at that time and some calculated values of EA and IP.

Johnson and Rohrlich[6] proposed another formula which used five or more parameters. Although much newer (1959) experimental data were available, their success with different elements was very widely varied, because the parameters were very sensitive to small errors in the experimental IP's of the positive ions.

Typically the estimates of the EA obtained by these extrapolation methods differ substantially depending upon the extrapolation formula used and the experimental data available. For Li, values ranging from 0.34 eV to 0.82 eV have been found.[1-3]

A second class of approximations[7,8] uses a consistent computational scheme to calculate the total energy of the members of the iso-electronic sequence for N and N-1 electron atoms and positive ions. A sequence of errors is then obtained by comparison with experiment and extrapolation of these errors is then used to estimate the EA. Because of the uncertainty in the extrapolation this approach is reliable only if the sequence of errors is sufficiently small and sufficiently smooth.

Weiss[9] has used a method of superposition of configurations (SOC) to calculate the detachment potentials for

alkali ions and other elements. The method consists of writing a trial function for the N electron system as a linear superposition of terms which include the ground state Hartree-Fock function and a number of elaborately obtained virtual excited orbitals. The calculation of the energies is carried out in a manner which produces approximately the same error in both systems. His results agree very well with experimental values.[10,11]

In the present work we calculate the energies of the N electron and the N-1 electron systems in a similar manner as Weiss,[9] but differing in the way of obtaining the virtual orbitals. The N-1 electron system is described by a single configuration of orbitals contained from an analytic Hartree-Fock description using a self-consistent V^{N-2} potential. The N electron system is described by a fixed core multiconfiguration Hartree-Fock wave function which uses the same orbitals obtained for the N-1 electron system. Details of this formalism are contained in Sec. I-2. Sec. I-3 discusses an application of this formalism to obtain the electron detachment potential of Li^- and Na^- and the ionization potential of Be.

The existence of states of compound nuclei made up of an excited target nucleus and an incident nucleon has long been known to give rise to the strong resonances found in nucleon-nucleus elastic scattering. Similar phenomena existing in atoms such as the sharp maxima in optical

absorption and the resonant peaks of cross section in electron scattering can equally well be explained by the compound or autoionization states in atoms. In Sec. I-4 we summarize the theory of the autoionization states of atoms then apply a projection formalism to compute these states for the e^--Li and e^--Na systems. Conclusions and a brief discussion are given in Sec. I-5.

I-2. MULTICONFIGURATION HARTREE-FOCK CALCULATION OF ENERGY

The present formalism follows closely the analysis of Salmona and Seaton[12] which was applied originally to scattering states of the electron-alkali atom system. Before discussing how configurations of the N-1 and N electron systems are constructed we detail the method used to obtain the analytic single particle states utilized in the mixing.

A. Single-Particle Orbitals

The single particle states used here are determined by diagonalizing (self-consistently) the N-2 electron closed shell Hartree-Fock Hamiltonian in the manner of Clementi.[13]

$$\langle u_\sigma^\gamma(i) | h_{HF}^{core}(i) | u_{\sigma'}^{\gamma'}(i) \rangle = E_\gamma \delta_{\sigma\sigma'} \delta_{\gamma\gamma'} , \qquad (1)$$

where E_γ are single-particle energies and

$$u_\sigma^\gamma(i) = u^\gamma(i) \chi_\sigma(i) , \qquad (2)$$

where χ_σ are the spin functions, the u_σ^γ are spin orbitals with spatial functions expanded in a set of Slater orbitals and spherical harmonics

$$u^{\gamma}(i) = Y_{\ell_\gamma m_\gamma}(i) \sum_k b_{\gamma k} f_{\gamma k}(i) \ . \tag{3}$$

The lowest orbitals of the appropriate species are identified as core orbitals and are determined in a self-consistent fashion. We label the core spin-orbitals by a_i, i=1···N-2. The Hartree-Fock Hamiltonian is then given by[14]

$$h_{HF}^{core} = -\nabla^2 - \frac{2Z}{r} + V\text{-}W \ , \tag{4}$$

where

$$V\ u_\sigma^{\gamma}(i) = \sum_{j=1}^{N-2} v(a_j,a_j)\ u_\sigma^{\gamma}(i) \ , \tag{5}$$

$$W\ u_\sigma^{\gamma}(i) = \sum_{j=1}^{N-2} v(a_j,u_\sigma^{\gamma})a_j(i) \ , \tag{6}$$

and

$$v(a_j,a_k) = 2 \int d\vec{r}\ a_j^{+}(\vec{r})\ a_k(\vec{r})/|\vec{r}-\vec{r}_i| \ . \tag{7}$$

The choice of the V^{N-2} approximation for the single particle states is made for two reasons. First we desire a reasonable single configuration representation of the ground and excited states of the N-1 electron system and these are best represented by the V^{N-2} approximation.

Further, as shown by Salmona and Seaton,[12] the formalism for describing the N electron system is materially simplified if the single particle orbitals diagonalize the core Hartree-Fock Hamiltonian.

The procedure used for choosing the Slater orbitals to be coupled in Eq. (3) is as follows. Although we self-consistently diagonalize in the V^{N-2} approximation the set of Slater orbitals which we use is that set obtained by Clementi[13] in the V^{N-1} approximation, augmented with additional Slater orbitals to better represent the lowest lying excited states of the valence electron. For those angular momentum species not included in the Clementi calculation we have simply chosen a reasonable basis set and in some cases have optimized parameters to obtain low lying excited valence states of these angular momentum species. In the present calculation only states with symmetry $\ell=0,1,2$ have been included.

B. The N-1 Electron System

The ground state and lowest lying excited states of the N-1 electron system are represented by the single configuration

$$\psi^{\gamma}(N-1) = D_{N-1}\ (a_1 a_2 \cdots a_{N-2}\ u_{\sigma}^{\gamma})\ , \tag{8}$$

where D_{N-1} is the determinantal function

$$D_{N-1}(a_1 a_2 \cdots a_{N-2}\, u_\sigma^\gamma) =$$

$$\frac{1}{\sqrt{(N-1)!}} \begin{vmatrix} a_1(1) a_2(1) -- a_{N-2}(1) & u_\sigma^\gamma(1) \\ a_1(2) & \vdots \\ \vdots & \\ a_1(N-1) ---------- & u_\sigma^\gamma(N-1) \end{vmatrix} . \qquad (9)$$

Here the a_i are the core spin-orbitals and $u_\sigma^\gamma \neq a_i$ is the single-particle valence spin-orbital (eg. for Li we have a_1=1s↑, a_2=1s↓, and $u_{\sigma=\uparrow}^\gamma$=2s↑, 2p↑, 3s↑,•••) obtained as described above. The assumption that the excited states of the N-1 electron system can be represented by single-particle excitations of the valence electron restricts the application to the lowest lying excited states. The wave function Eq. (8) is an eigenstate of orbital angular momentum $L=\ell_\gamma$, $M=m_\gamma$, spin angular momentum $S=\frac{1}{2}$, $M_S=\sigma$, and parity $\pi=(-1)^L$.

To simplify later calculations, the following orthonormal conditions are imposed:

$$\langle a_i | a_j \rangle = \delta_{ij} \ ,$$

$$\langle a_i | u_\sigma^\gamma \rangle = 0 \ , \qquad i,j = 1,2,\cdots N-2 \text{ and all } \gamma,\gamma',\sigma,\sigma' \ .$$

$$\langle u_\sigma^{\gamma'} | u_\sigma^\gamma \rangle = \delta_{\gamma\gamma'} \ \delta_{\sigma\sigma'} \ ,$$

Since adding a multiple of one column to another in a determinant does not change the value of the determinant, the above conditions do not change the wave functions.

C. The N Electron System

We describe the N electron system by a fixed closed core of N-2 electrons with the multiconfiguration mixing of states of the valence and binding electrons

$$\Psi^\Gamma(N) = N \sum_{\gamma\sigma}\sum C(\tfrac{1}{2}\tfrac{1}{2}S;\sigma-\sigma 0) \ C(\ell_1\ell_2 L;m_1 m_2 M) \times D_N(a_1 a_2 \cdots a_{N-2} \ u_\sigma^\gamma \ \phi_{-\sigma}^\gamma) \ . \qquad (10)$$

Here N is the normalization constant and γ is the valence state. The states chosen to be coupled are such that Ψ^Γ is an eigenstate of L, S, M, M_S=0, and $\pi=(-1)^L$. We impose $\langle a_i | \phi_\sigma^\gamma \rangle$=0 to simplify computation. No other conditions are imposed on u_σ^γ or $\phi_{-\sigma}^{\gamma'}$, thus, in general, $\langle u_\sigma^\gamma | \phi_\sigma^{\gamma'} \rangle \neq 0$. For singlet states, this allows the valence and binding electrons to have the same space orbital.

The non-relativistic Hamiltonian is given by

$$H(N) = \sum_{i=1}^{N} f(i) + \sum_{i>j=1}^{N} g(i,j) , \tag{11}$$

where

$$f(i) = -\nabla^2(i) - \frac{2Z}{r_i} , \tag{12}$$

and

$$g(i,j) = 2/r_{ij} . \tag{13}$$

The functional $\langle \Psi^{\Gamma} | H-E | \Psi^{\Gamma} \rangle$ is then constructed and is simplified in the following manner.

We first consider the matrix elements of $\langle D^{\gamma'\sigma'} | F | D^{\gamma\sigma} \rangle$, where the D's have the form of Eq. (10) and F is single-particle, two-particle, or constant multiplier operators. Condon and Shortley[15] have discussed a method of evaluating integrals involving products of two determinantal functions in each of which all elements are mutually orthonormal. Because of the fact that, in general $\langle u^{\gamma'} | \phi^{\gamma} \rangle \neq 0$, some modifications of the method are necessary (see Appendix I). With this modified method, the following results are obtained. In order to express the results in a more general form, the orthonormality relation, $\langle u^{\gamma'}_{\sigma'} | u^{\gamma}_{\sigma} \rangle = \delta_{\gamma\gamma'}\delta_{\sigma\sigma'}$, is not utilized at this stage.

(1) $F = 1$.

$$\langle D^{\gamma'\sigma'}|F|D^{\gamma\sigma}\rangle = \langle D^{\gamma'\sigma'}|D^{\gamma\sigma}\rangle$$

$$= \langle u_\sigma^{\gamma'}|u_\sigma^{\gamma}\rangle\langle\phi_{-\sigma}^{\gamma'}|\phi_{-\sigma}^{\gamma}\rangle - \langle u_\sigma^{\gamma'}|\phi_{-\sigma}^{\gamma}\rangle\langle\phi_{-\sigma}^{\gamma'}|u_\sigma^{\gamma}\rangle. \tag{14}$$

(2) $F = \sum_{i=1}^{N} f(i)$.

$$\langle D^{\gamma'\sigma'}|F|D^{\gamma\sigma}\rangle$$

$$= \sum_{i=1}^{N-2} \langle a_i|f|a_i\rangle\{\langle\phi_{-\sigma}^{\gamma'}|\phi_{-\sigma}^{\gamma}\rangle\langle u_\sigma^{\gamma'}|u_\sigma^{\gamma}\rangle$$

$$- \langle\phi_{-\sigma}^{\gamma'}|u_\sigma^{\gamma}\rangle\langle u_\sigma^{\gamma'}|\phi_{-\sigma}^{\gamma}\rangle\} + \langle\phi_{-\sigma}^{\gamma'}|\phi_{-\sigma}^{\gamma}\rangle\langle u_\sigma^{\gamma'}|f|u_\sigma^{\gamma}\rangle$$

$$+ \langle\phi_{-\sigma}^{\gamma'}|f|\phi_{-\sigma}^{\gamma}\rangle\langle u_\sigma^{\gamma'}|u_\sigma^{\gamma}\rangle - \langle\phi_{-\sigma}^{\gamma'}|u_\sigma^{\gamma}\rangle\langle u_\sigma^{\gamma'}|f|\phi_{-\sigma}^{\gamma}\rangle$$

$$- \langle\phi_{-\sigma}^{\gamma'}|f|u_\sigma^{\gamma}\rangle\langle u_\sigma^{\gamma'}|\phi_{-\sigma}^{\gamma}\rangle. \tag{15}$$

(3) $F = \sum_{i>j=1}^{N} g(i,j)$.

$$\langle D^{\gamma'\sigma'}|F|D^{\gamma\sigma}\rangle$$

$$= \sum_{i>j=1}^{N-2} \{\langle a_i a_j|g|a_i a_j\rangle - \langle a_i a_j|g|a_j a_i\rangle\}$$

$$\times \{\langle u_\sigma^{\gamma'}, | u_\sigma^{\gamma}\rangle\langle \phi_{-\sigma}^{\gamma'}, | \phi_{-\sigma}^{\gamma}\rangle - \langle u_\sigma^{\gamma'}, | \phi_{-\sigma}^{\gamma}\rangle\langle \phi_{-\sigma}^{\gamma'}, | u_\sigma^{\gamma}\rangle\}$$

$$+ \langle u_\sigma^{\gamma'}, \phi_{-\sigma}^{\gamma'} | g | u_\sigma^{\gamma}\phi_{-\sigma}^{\gamma}\rangle - \langle u_\sigma^{\gamma'}, \phi_{-\sigma}^{\gamma'}, | g | \phi_{-\sigma}^{\gamma}u_\sigma^{\gamma}\rangle$$

$$+ \sum_{i=1}^{N-2} \{\langle a_i\phi_{-\sigma}^{\gamma'}, | g | a_i\phi_{-\sigma}^{\gamma}\rangle\langle u_\sigma^{\gamma'}, | u_\sigma^{\gamma}\rangle$$

$$+ \langle a_i u_\sigma^{\gamma'}, | g | a_i u_\sigma^{\gamma}\rangle\langle \phi_{-\sigma}^{\gamma'}, | \phi_{-\sigma}^{\gamma}\rangle$$

$$- \langle a_i\phi_{-\sigma}^{\gamma'}, | g | a_i u_\sigma^{\gamma}\rangle\langle u_\sigma^{\gamma'}, | \phi_{-\sigma}^{\gamma}\rangle$$

$$- \langle a_i u_\sigma^{\gamma'}, | g | a_i\phi_{-\sigma}^{\gamma}\rangle\langle \phi_{-\sigma}^{\gamma'}, | u_\sigma^{\gamma}\rangle$$

$$- \langle a_i\phi_{-\sigma}^{\gamma'}, | g | \phi_{-\sigma}^{\gamma}a_i\rangle\langle u_\sigma^{\gamma'}, | u_\sigma^{\gamma}\rangle$$

$$- \langle a_i u_\sigma^{\gamma'}, | g | u_\sigma^{\gamma}a_i\rangle\langle \phi_{-\sigma}^{\gamma'}, | \phi_{-\sigma}^{\gamma}\rangle$$

$$+ \langle a_i\phi_{-\sigma}^{\gamma'}, | g | u_\sigma^{\gamma}a_i\rangle\langle u_\sigma^{\gamma'}, | \phi_{-\sigma}^{\gamma}\rangle$$

$$+ \langle a_i u_\sigma^{\gamma'}, | g | \phi_{-\sigma}^{\gamma}a_i\rangle\langle \phi_{-\sigma}^{\gamma'}, | u_\sigma^{\gamma}\rangle\} \quad . \tag{16}$$

Note that in performing the spin sums, restrictions must be imposed on the spins in order that the exchange terms do not vanish. For example, in Eq. (16), the last four terms yield, respectively,

$$\sigma' = \sigma = -\sigma_i \ ,$$

$$\sigma' = \sigma = \sigma_i \ ,$$

$$\sigma' = -\sigma = -\sigma_i \ ,$$

$$\sigma' = -\sigma = \sigma_i \ .$$

Therefore, only (N-2)/2 terms contribute in the sum over i (for example, if 1s↑ contributes, then 1s↓ does not, etc.). To remind ourselves of this fact we shall denote such a sum by Σ'.

The relations

$$C(\tfrac{1}{2}\tfrac{1}{2}S;\sigma-\sigma 0) = (-1)^{S+1}\, C(\tfrac{1}{2}\tfrac{1}{2}S;-\sigma\sigma 0)$$

and

$$\sum_{\sigma} C^2(\tfrac{1}{2}\tfrac{1}{2}S;\sigma-\sigma 0) = 1$$

are used to perform the spin sums. We obtain the following equation in which the a_i's stand for spinless core orbitals.

$$\sum_{\sigma\sigma'} C(\tfrac{1}{2}\tfrac{1}{2}S;\sigma-\sigma 0)\; C(\tfrac{1}{2}\tfrac{1}{2}S;\sigma'-\sigma' 0)\; \langle D^{\gamma'\sigma'}|H-E|D^{\gamma\sigma}\rangle$$

$$= \langle D^{\gamma'}|H-E|D^{\gamma}\rangle$$

$$= [\langle u^{\gamma'}|u^{\gamma}\rangle\langle\phi^{\gamma'}|\phi^{\gamma}\rangle + (-1)^{S}\langle u^{\gamma'}|\phi^{\gamma}\rangle\langle\phi^{\gamma'}|u^{\gamma}\rangle]$$

$$x\ [-E + \sum_{i>j}^{N-2}\langle a_i a_j|g|a_i a_j\rangle - \sum_{i>j}^{N-2}{}'\langle a_i a_j|g|a_j a_i\rangle$$

$$+ \sum_{i}^{N-2}\langle a_i|f|a_i\rangle] + \langle\phi^{\gamma'}|\phi^{\gamma}\rangle\{\langle u^{\gamma'}|f|u^{\gamma}\rangle$$

$$+ \sum_{i=1}^{N-2}\langle a_i u^{\gamma'}|g|a_i u^{\gamma}\rangle \sum_{i=1}^{N-2}{}'\langle a_i u^{\gamma'}|g|u^{\gamma}a_i\rangle\}$$

$$+ \langle u^{\gamma'}|u^{\gamma}\rangle\ \{\langle\phi^{\gamma'}|f|\phi^{\gamma}\rangle + \sum_{i}^{N-2}\langle a_i\phi^{\gamma'}|g|a_i\phi^{\gamma}\rangle$$

$$- \sum_{i}^{N-2}{}'\langle a_i\phi^{\gamma'}|g|\phi^{\gamma}a_i\rangle\} + (-1)^{S}\{\langle\phi^{\gamma'}|u^{\gamma}\rangle\langle u^{\gamma'}|f|\phi^{\gamma}\rangle$$

$$+ \langle u^{\gamma'}|\phi^{\gamma}\rangle\langle\phi^{\gamma'}|f|u^{\gamma}\rangle + \langle u^{\gamma'}\phi^{\gamma'}|g|\phi^{\gamma}u^{\gamma}\rangle$$

$$+ \langle u^{\gamma'}|\phi^{\gamma}\rangle\ [\sum_{i}^{N-2}\langle a_i\phi^{\gamma'}|g|a_i u^{\gamma}\rangle$$

$$- \sum_{i}^{N-2}{}'\langle a_i\phi^{\gamma'}|g|u^{\gamma}a_i\rangle] + \langle\phi^{\gamma'}|u^{\gamma}\rangle$$

$$[\sum_{i}^{N-2}\langle a_i u^{\gamma'}|g|a_i\phi^{\gamma}\rangle - \sum_{i}^{N-2}{}'\langle a_i u^{\gamma'}|g|\phi^{\gamma}a_i\rangle]\}$$

$$+ \langle u^{\gamma'}\phi^{\gamma'}|g|u^{\gamma}\phi^{\gamma}\rangle\ . \qquad (17)$$

We now observe that the Hartree-Fock Hamiltonian defined by Eq. (4) and the energy for the alkali core are given by

$$h_{HF}^{core}(j)\psi(j) = f(j)\psi(j) + \sum_{i}^{N-2} \langle a_i(k)|g(k,j)|a_i(k)\rangle$$

$$|\psi(j)\rangle - \sum_{i}^{N-2}{}' \; |a_i(j)\rangle\langle a_i(k)|g(k,j)|\psi(j)\rangle \,, \qquad (4')$$

and

$$E_{HF}^{core} = \sum_{i}^{N-2} \langle a_i(k)|f(k)|a_i(k)\rangle$$

$$+ \sum_{i>j}^{N-2} \langle a_i(1)a_j(2)|g(1,2)|a_i(1)a_j(2)\rangle$$

$$- \sum_{i>j}^{N-2}{}' \langle a_i(1)a_j(2)|g(1,2)|a_j(1)a_i(2)\rangle \,. \qquad (18)$$

Recalling Eq. (1),

$$\langle u^{\gamma'}|h_{HF}^{core}|u^{\gamma}\rangle = E_{\gamma}\delta_{\gamma'\gamma} \,. \qquad (1')$$

We have:

$$\langle D^{\gamma'}|H-E|D^{\gamma}\rangle = \delta_{\gamma\gamma'}\langle\phi^{\gamma'}|h_{HF}^{core} - (E-E_{HF}^{core}-E_{\gamma})|\phi^{\gamma}\rangle$$

$$+ \langle u^{\gamma'}\phi^{\gamma'}|g|u^{\gamma}\phi^{\gamma}\rangle + (-1)^{S}\{\langle u^{\gamma'}\phi^{\gamma'}|h_{HF}^{core}(1)$$

$$+ h_{HF}^{core}(2) - (E-E_{HF}^{core})|\phi^{\gamma}u^{\gamma}\rangle + \langle u^{\gamma'}\phi^{\gamma'}|g|\phi^{\gamma}u^{\gamma}\rangle\},$$

(19)

In performing the sum over m, we define:

$$u^{\gamma}(\vec{r}) = u^{\gamma}(r)\ Y_{\ell_1 m_1}(\hat{r}) \ , \tag{20}$$

$$\phi^{\gamma}(\vec{r}) = \phi^{\gamma}(r)\ Y_{\ell_2 m_2}(\hat{r}) \ , \tag{21}$$

$$P_{\lambda}(\Omega_{12}) = \frac{4\pi}{2\lambda+1} \sum_{\mu} Y^{*}_{\lambda\mu}(\hat{r}_1)\ Y_{\lambda\mu}(\hat{r}_2) \ , \tag{22}$$

$$S_{\lambda}(1,2) = r_{<}^{\lambda}/r_{>}^{\lambda+1} \ , \tag{23}$$

$$Y^{M}_{L\ell_1\ell_2}(\Omega_{12}) = \sum_{m_1 m_2} C(\ell_1\ell_2 L; m_1 m_2 M) Y_{\ell_1 m_1}(\hat{r}_1) Y_{\ell_2 m_2}(\hat{r}_2) . \tag{24}$$

Then:

$$g(1,2) = 2 \sum_{\lambda=0}^{\infty} S_{\lambda}(1,2)\ P_{\lambda}(\Omega_{12}) \ , \tag{25}$$

$$\langle Y^{M}_{L\ell_1'\ell_2'}(\Omega_{12}) | Y^{M}_{L\ell_1\ell_2}(\Omega_{12})\rangle = \delta_{\ell_1\ell_1'}\ \delta_{\ell_2\ell_2'} \ , \tag{26}$$

$$\langle Y^{M}_{L\ell_1'\ell_2'}(\Omega_{12}) | Y^{M}_{L\ell_1\ell_2}(\Omega_{21})\rangle = (-1)^{\ell_1'+\ell_2'-L}\ \delta_{\ell_1\ell_2'}\ \delta_{\ell_2\ell_1'} \ , \tag{27}$$

$$\langle Y^{M}_{L\ell_1'\ell_2'}(\Omega_{12}) | P_{\lambda} | Y^{M}_{L\ell_1\ell_2}(\Omega_{12})\rangle = f_{\lambda}(\ell_1'\ell_2'\ell_1\ell_2;L) , \tag{28}$$

$$\langle Y^M_{L\ell_1'\ell_2'}(\Omega_{12})|P_\lambda|Y^M_{L\ell_1\ell_2}(\Omega_{21})\rangle = (-1)^{\ell_1'+\ell_2'-L}$$

$$\times f_\lambda(\ell_1'\ell_2'\ell_2\ell_1;L) \ , \tag{29}$$

where the angular factor f is given by Percival and Seaton.[16] We have:

$$\langle\Psi^\Gamma|H-E|\Psi^\Gamma\rangle = N^2 \sum_{\gamma\gamma'} \{\delta_{\gamma\gamma'}\delta_{\ell_1\ell_1'}\delta_{\ell_2\ell_2'}\langle\phi^{\gamma'}|h_{HF}^{(\ell_2)}$$

$$- (E-E_{HF}^{core}-E_\gamma)|\phi^\gamma\rangle + e^2 \sum_\lambda f_\lambda(\ell_1'\ell_2'\ell_1\ell_2;L)$$

$$\times \langle u^{\gamma'}\phi^{\gamma'}|S_\lambda|u^\gamma\phi^\gamma\rangle + (-1)^{S+\ell_1+\ell_2-L}$$

$$\times [\delta_{\ell_1'\ell_2}\delta_{\ell_2'\ell_1}\langle u^{\gamma'}\phi^{\gamma'}|h_{HF}^{(\ell_2)}(1) + h_{HF}^{(\ell_1)}(2)$$

$$- (E-E_{HF}^{core})|\phi^\gamma u^\gamma\rangle + e^2 \sum_\lambda f_\lambda(\ell_1'\ell_2'\ell_2\ell_1;L)$$

$$\times \langle u^{\gamma'}\phi^{\gamma'}|S_\lambda|\phi^\gamma u^\gamma\rangle]\} \ , \tag{30}$$

where

$$N^{-2} = \sum_{\gamma\gamma'} \{\delta_{\gamma\gamma'}\delta_{\ell_1\ell_1'}\delta_{\ell_2\ell_2'}\langle\phi^{\gamma'}|\phi^\gamma\rangle\langle u^{\gamma'}|u^\gamma\rangle$$

$$+ (-1)^{S+\ell_1+\ell_2-L}\delta_{\ell_1\ell_2'}\delta_{\ell_2\ell_1'}\langle\phi^{\gamma'}|u^\gamma\rangle\langle u^{\gamma'}|\phi^\gamma\rangle\} \ , \tag{31}$$

and

$$h_{HF}^{(\ell)} = -\frac{d^2}{dr^2} + \frac{\ell(\ell+1)}{r^2} - \frac{Ze^2}{r} + (V-W)_{core} \ . \qquad (32)$$

If we choose arbitrary Slater orbitals as bases for an expansion of the radial wave functions, ϕ^{γ}, the orthogonalization process to make $<a_i|\phi^{\gamma}>=0$ may be quite tedious. This process can be made unnecessary, however, if we simply express ϕ^{ν} in terms of u^{γ}, Eq. (3),

$$\phi^{\nu} = \sum_{\gamma} C_{\gamma\nu} u^{\gamma} \ . \qquad (33)$$

Thus we see one of the advantages of using the same single-particle states for both the N-1 and N electron systems. It also eliminated the extra work of generating the virtual excited orbitals as done by Weiss.[9] Further, ϕ^{ν} can also be easily made orthogonal to Hartree-Fock representation of any of the lowest lying excited states of the N-1 electron system obtained above by simply restricting the summations over γ to exclude the state desired.

Using Eq. (33) and the orthonormality relation $<u^{\gamma'}|u^{\gamma}>=\delta_{\gamma',\gamma}$, (also note that $\ell_1+\ell_2-L$=even), Eq. (30) can further be simplified:

$$<\Psi^{\Gamma}|H-E|\Psi^{\Gamma}> = N^2 \sum_{\gamma\nu} C_{\gamma\nu} \sum_{\gamma'\nu'} C_{\gamma'\nu'}$$

$$x \{[E_{HF}^{core}+E_\gamma+E_\nu-E] (\delta_{\gamma\gamma'}\delta_{\nu\nu'}+(-1)^S\delta_{\gamma\nu'}\delta_{\nu\gamma'})$$

$$+ 2 \sum_\lambda f_\lambda(\ell_\gamma,\ell_\nu,\ell_\gamma\ell_\nu;L) \langle u^{\gamma'}u^{\nu'}|S_\lambda|u^\gamma u^\nu\rangle$$

$$+ 2(-1)^S \sum_\lambda f_\lambda(\ell_\gamma,\ell_\nu,\ell_\nu\ell_\gamma;L) \langle u^{\gamma'}u^{\nu'}|S_\lambda|u^\nu u^\gamma\rangle\} ,$$

(34)

and

$$N^{-2} = \sum_{\gamma\nu} \sum_{\gamma'\nu'} C_{\gamma\nu} C_{\gamma'\nu'} [\delta_{\gamma\gamma'}\delta_{\nu\nu'}+(-1)^S\delta_{\gamma\nu'}\delta_{\nu\gamma'}] .$$

(35)

We note that Eq. (34) takes this particularly simple form only if the single-particle states are obtained from Eq. (1). Eq. (34) can be written in the matrix form:

$$\sum_{\alpha\beta} C_\alpha [H_{\alpha\beta}-E\, S_{\alpha\beta}] C_\beta = 0 , \qquad (36)$$

where H and S are the Hamiltonian and overlap matrix elements on the basis of functions $u^\gamma(1)$, $u^\nu(2)$ of Eq. (3), and $\alpha=(\gamma,\nu)$, $\beta=(\gamma',\nu')$. The variational principle gives:

$$\sum_\beta [H_{\alpha\beta}-E\, S_{\alpha\beta}] C_\beta = 0 . \qquad (37)$$

Standard techniques are used to solve this matrix eigenvalue problem.

We conclude this section by noting that the single configuration approximation for the Ψ^{γ} (N-1) electron state has an energy $E_{HF}^{core}+E_{\gamma}$.

I-3. DETACHMENT POTENTIALS OF Be, Li^- AND Na^-

A. The Ionization Potential of Be

As a test of the present formalism we have considered the ionization potential of Be, a quantity which has been determined quite accurately both experimentally and theoretically. The single-particle states generated from Eq. (1) diagonalize the Be^{++} Hartree-Fock Hamiltonian. The Slater basis functions of Eq. (3) take the form

$$f_{\gamma k}(r) = N_{\gamma k}\, r^{n_k-1}\, e^{-\chi_k r}$$

$$N_{\gamma k} = (2\chi_k)^{n_k+0.5}/[(2n_k)!]^{\frac{1}{2}} \qquad (38)$$

where $N_{\gamma k}$ is a normalization factor and the parameters n_k, χ_k for a given angular momentum species are listed in Table II. (Also included in Table II are coefficients $b_{\gamma k}$ of Eq. (3) for the two lowest states of each momentum species and the total energy obtained in this work as well as those of Clementi.[13]) We have used 10(8,5) orbitals for s(p,d) species. The energy eigenvalues, E_γ of Eq. (1) are given in Table III. The eigenvector associated with the lowest energy s state is identified with the 1s orbital and is treated self-consistently. We label the eigenstates of Eq. (1) by 1s, 2s,·····10s; 2p, 3p,···9p; 3d, 4d,···7d in order of increasing energies. However we

note that only those states $n\ell$ with $n \leq 4$ can be considered to be reasonable Hartree-Fock approximations to the hydrogen-like excited states of the valence electron. Although all eigenstates are localized some have energies in the continuum. This is desirable because it is known that the mixing of continuum-like states is important to obtain good energies.[17]

The Hartree-Fock energy for the $1s^2 2s^2 S$ configuration of Be^+ is found to be -28.55472 Ry. This is to be compared with the essentially exact value of -28.64958 Ry.[7] Approximately 90% of this difference is due to the correlation energy between the 1s electrons with the remainder due to the correlation between the 2s and 1s electrons.[18] The essential feature of the present calculation is that one expects essentially the same error in the core correlation energy and the valence electron-core correlation energy when the "binding" electron is added to give an N electron system if the same single particle states are used for both the N-1 and N electron systems.

The energy of the ^1S ground state of Be was computed using Eq. (34) with a mixing of 34 configurations for the outer two electrons which included

$$\gamma\nu(S) = 2s^2, 2s3s, \cdots 2s8s; 3s^2; \cdots 3s8s; 4s^2;$$

$$2p^2, \cdots 2p8p; 3p^2, \cdots 3p8p; 4p^2; 3d^2, \cdots 3d7d; 4d^2 \tag{39}$$

The energy computed in this manner was found to be -29.23665 Ry. Taking the difference between this value and the Hartree-Fock energy of Be^+ computed here we obtain an ionization potential for Be of 0.68193 Ry. This is in good agreement with the essentially exact value of 0.68524 Ry. which is obtained by adding to the precise two-electron ion energy results of Pekeris[19] the experimental ionization energies,[11] relativistically corrected. This suggests that our basic assumption of cancelling errors in the energies computed in the manner described above is well founded for systems with two electrons outside a closed core.

B. The Electron Affinity of Li

The procedure followed for computing the energies of Li and Li^- is precisely the same as above. Table IV gives the parameters of the Slater basis functions, eigenvalues and eigenvectors of the two lowest lying states for each momentum species as obtained by this work as well as those obtained by Clementi.[13] Eigenvalues for higher states are given in Table III. The Hartree-Fock energy for the $1s^2 2s\ ^2S$ configuration of Li was found to be -14.86544 Ry. in good agreement with previous calculations.[13,20] The configurations listed in Eq. (39) were mixed and an energy of -14.91049 Ry. was obtained for Li^-. This corresponds to an electron affinity of 0.04505 Ry.

TABLE II: PARAMETERS OF BASIS FUNCTIONS FOR Be^+

(A) $\ell=0$

n_k	χ_k	This Work -28.55472* 1s -11.33418#	This Work -28.55472* 2s -1.33213$	Clementi[13] -28.55466* 1s -10.27718#	Clementi[13] -28.55466* 2s -1.33228$
1	6.96969	0.05214	-0.00842	0.06476	-0.01189
1	4.80000	0.05085	-0.01315	-	-
1	3.49627	0.89650	-0.19691	0.94315	-0.21123
2	2.50092	0.01826	-0.15573	-0.00058	-0.15198
2	1.29671	-0.02095	0.51691	0.01560	0.53054
2	1.11089	0.01736	0.62066	0.01070	0.60118
2	0.60000	-0.00182	-0.00685	-	-
2	0.25000	0.00028	0.00068	-	-
2	0.05000	-0.00003	-0.00006	-	-
2	0.00100	0.00000	0.00000	-	-

* Total energy, shown only in table for $\ell=0$.

\# 1s single-particle energy.

$ 2s single-particle energy.

Note: The same format is used for the p- and d-states and for Tables IV and VII.

TABLE II: (CONTINUATION)

(B) ℓ=1

n_k	χ_k	2p -1.03881	3p -0.45650
2	3.50000	0.02870	-0.07093
2	2.50000	-0.01573	0.34728
2	1.80000	0.00653	-0.96978
2	1.20000	0.45272	2.80067
2	0.90000	0.62362	-6.12418
2	0.67000	-0.07981	4.38892
2	0.20000	0.00154	0.03838
2	0.00100	-0.00000	-0.00000

(C) ℓ=2

n_k	χ_k	3d -0.44286	4d -0.22450
3	2.50000	0.02948	-0.09672
3	1.50000	-0.15729	0.52350
3	0.90000	0.65370	-1.76330
3	0.50000	0.51722	1.38191
3	0.15000	-0.02980	0.27624

TABLE III: SINGLE PARTICLE EIGENVALUES E_γ IN THE V^{N-2} APPROXIMATION FOR Be^+, Li AND Na

	Be	Li^-	Na^-
1s	-11.33418	-5.58472	-81.51944
2s	-1.33213	-0.39261	-6.14736
3s	-0.53294	-0.14693	-0.36362
4s	-0.27541	-0.07167	-0.14011
5s	-0.08887	-0.03250	-0.05731
6s	-0.00200	-0.00100	0.08820
7s	0.12485	0.16567	1.66161
8s	3.37051	1.86378	8.93712
9s	19.87050	10.01469	36.20718
10s	132.69202	62.97964	161.38448
2p	-1.03881	-0.25727	-3.59437
3p	-0.45650	-0.11302	-0.21835
4p	-0.24094	-0.06002	-0.10045
5p	-0.03496	-0.00100	0.00303
6p	-0.00200	0.03700	1.11334
7p	1.16730	0.60414	5.90755
8p	5.57627	2.99675	21.20926
9p	25.47377	16.21537	79.89123
3d	-0.44286	-0.11112	-0.11133
4d	-0.22450	-0.05175	-0.05145
5d	-0.14269	0.01757	0.06437
6d	0.74269	0.84610	1.28819
7d	6.20990	6.21842	7.20673

(0.613 eV). This is in agreement with the calculated value of 0.62 eV by Weiss[9] and the measured value of 0.6 eV by Ya'akobi.[10]

Subsidiary calculations were performed in which only some of the configurations listed in Eq. (39) were mixed. We give results for n=1($2s^2$), n=7($2s^2\cdots 2s8s$), n=14 ($2s^2\cdots 2s8s; 2p^2\cdots 2p8p$) and n=34. The results are presented in Table V. As is well known a single configuration does not bind the negative alkali ion even in the Hartree-Fock approximation using a self-consistent V^N potential.[8] As indicated by the n=7 results one can just bind Li^- in the Hartree-Fock approximation by placing the outer two electrons in inequivalent orbitals. The 2s-2p coupling alone gives 99.7% (0.04490 Ry.) of the total electron affinity. This agrees well with the fact that the 2s-2p interaction contributes 99% of the total polarizability of Li.[21]

The contribution of the polarizability from virtual excitations of the 2s state in the Hartree-Fock approximation is given by[22]:

$$\alpha_{Li} = \frac{4}{3} \sum_{n=2}^{\infty} M_n^2/(E_{np}-E_{2s}) \ , \tag{40}$$

where

$$M_n = \langle u_{2s}(r)|r|u_{np}(r)\rangle \ . \tag{41}$$

The total polarizability of Li and the contributions from different states np are given in Table VI.

We have also investigated the Li^- system in the ^3S, $^{1,3}P$, $^{1,3}D$ states and find, as anticipated, that it does not bind. The configurations included 31 terms for P and 33 terms for D and are given below

$$\gamma\nu(P) \quad 2s2p,2s3p,\cdots 2s8p;3s2p\cdots 3s8p;$$
$$4s2p\cdots 4s4p;2p5s\cdots 2p8s;$$
$$3d2p\cdots 3d4p;4d2p\cdots 4d4p \ . \qquad (42)$$

$$\gamma\nu(D) \quad 2s3d,2s4d\cdots 2s6d;3s3d,\cdots 3s6d;4s3d\cdots 4s6d;$$
$$2p2p\cdots 2p8p;3p3p\cdots 3p8p;4p4p;3d3d,\cdots 3d6d;$$
$$4d4d\cdots 4d6d \ . \qquad (43)$$

Upon request from A. K. Rajagopal, we investigated the possibility of the existence of bound states of a positron in a Li atom. The result was negative as we anticipated.

C. The Electron Affinity of Na

For Na we have proceeded in a manner similar to the Be calculation. However we must now self-consistently solve for the 1s, 2s and 2p orbitals in the core. We have augmented the Clementi Slater orbitals with only two additional orbitals of the s species and three additional

TABLE IV: PARAMETERS OF BASIS FUNCTIONS FOR Li

(A) ℓ=0

n_k	χ_k	This Work -14.86544		Clementi[13] -14.86545	
		1s	2s	1s	2s
		-5.58472	-0.39261	-4.95550	-0.39264
1	4.70710	0.11040	-0.01401	0.11031	-0.01584
1	3.50000	0.00030	-0.00542	-	-
1	2.48030	0.89815	-0.13825	0.89778	-0.14426
2	1.73500	0.00875	-0.09246	0.00937	-0.08964
2	1.00000	-0.00233	0.09396	-0.00144	0.09077
2	0.66000	0.00098	0.97670	0.00109	0.97901
2	0.35000	-0.00019	0.00278	-0.00006	0.00202
2	0.10000	0.00003	-0.00016	-	-
2	0.05000	-0.00002	0.00006	-	-
2	0.00100	0.00000	-0.00000	-	-

Note: See footnote of Table II.

TABLE IV: (CONTINUATION)

(B) $\ell=1$

n_k	χ_k	2p -0.25727	3p -0.11302
2	3.50000	0.00427	-0.00982
2	1.80000	0.01848	0.06091
2	1.00000	-0.01046	-0.65994
2	0.71109	0.10683	2.06701
2	0.49782	0.91543	-4.19212
2	0.33300	-0.01719	3.05854
2	0.10000	0.00052	0.08339
2	0.00100	-0.00000	-0.00001

(C) $\ell=2$

n_k	χ_k	3d -0.11112	4d -0.05175
3	2.50000	0.00026	-0.00575
3	1.20000	-0.00021	0.03738
3	0.60000	0.00174	-0.16870
3	0.33300	0.99885	-0.19235
3	0.10000	-0.00034	1.02129

TABLE V: CONVERGENCE OF THE ELECTRON AFFINITY OF Li

n	Electron Affinity (Ry.)
1	-.07535
7	.00657
14	.04490
34	.04505

TABLE VI: POLARIZABILITY OF Li

Coupling	Polarizability	Total
2s-2p	167.29693	167.29693
2s-3p	0.18928	167.48621
2s-4p	0.08811	167.57432
2s-5p	0.00000	167.57432
2s-6p	0.91391	168.48823
2s-7p	0.47267	168.96089
2s-8p	0.01921	168.98010
2s-9p	0.00019	168.98029

Experimental value of the total polarizability is 148.5 ± 13.5.[21]

orbitals of the p species. Therefore the low lying excited valence states are not as well represented as they are for Be^+ or Li. The Slater parameters and single particle energies are given in Tables VII and III. The Hartree-Fock energy for the $1s^2 2s^2 2p^6 3s\ ^2S$ configuration of Na was found to be -323.71749 Ry. which is to be compared with the value -323.71778 Ry. obtained by Clementi[13] using single particle orbitals of the V^{N-1} approximation. The mixing of 34 configurations (Eq. (39) with $ns \rightarrow (n+1)s$, $np \rightarrow (n+1)p$) yielded an energy of -323.75690 Ry. for Na^- from which we compute an electron affinity of 0.03941 Ry. (0.536 eV). This is to be compared with the value of 0.54 eV of Weiss.[9]

The total poarizability of Na and the contributions from different p-states are also calculated and are presented in Table VIII.

TABLE VII: PARAMETERS OF BASIS FUNCTIONS FOR Na

(A) $\ell=0$

		This Work			Clementi[13]		
		-323.71749			-323.71778		
n_k	χ_k	1s	2s	3s	1s	2s	3s
		-81.51944	-6.14736	-0.36362	-80.95698	-5.59404	-0.36422
1	11.00000	0.96305	-0.23503	0.03505	0.96305	-0.23508	0.03532
3	12.36850	0.04218	-0.00375	0.00085	0.04219	-0.00373	0.00087
3	8.02540	0.01596	0.13140	-0.02214	0.01590	0.13129	-0.02237
3	5.70590	-0.00286	0.40151	-0.06238	-0.00281	0.40213	-0.06277
3	3.63100	0.00163	0.52747	-0.09330	0.00159	0.52699	-0.09421
3	2.15370	-0.00036	0.04775	0.00162	-0.00033	0.04726	0.00254
3	1.10810	0.00016	-0.00738	0.41288	0.00013	-0.00585	0.41486
3	0.70830	-0.00008	0.00323	0.63771	-0.00005	0.00217	0.63607
3	0.35000	0.00002	-0.00066	0.00107	-	-	-
3	0.10000	-0.00000	0.00009	0.00007	-	-	-

Note: See footnote of Table II.

TABLE VII: (CONTINUATION)

(B) ℓ=1

n_k	χ_k	This Work 2p	This Work 3p	Clementi[13] 2p	Clementi[13] 3p
		-3.59437	-0.21835	-3.03626	-
2	5.50000	0.47426	-0.04708	0.47360	-
4	8.39370	0.03581	-0.00333	0.03555	-
4	5.42060	0.27777	-0.02593	0.27825	-
4	3.56460	0.32520	-0.02911	0.32310	-
4	2.28330	0.06976	0.03483	0.07308	-
4	1.00000	-0.00253	0.56319	-	-
4	0.50000	0.00153	0.65161	-	-
4	0.33300	-0.00078	-0.15675	-	-

(C) ℓ=2

n_k	χ_k	3d	4d
		-0.11133	-0.05145
3	3.20000	-0.00175	-0.00324
3	1.50000	-0.00236	0.01336
3	0.70000	-0.00512	-0.06681
3	0.33300	-0.99667	-0.27237
3	0.10000	0.00103	1.03886

TABLE VIII: POLARIZABILITY OF Na

Coupling	Polarizability	Total
3s-3p	186.93607	186.93607
3s-4p	0.74289	187.67896
3s-5p	0.15197	187.83092
3s-6p	0.08467	187.91559
3s-7p	0.00015	187.91576
3s-8p	0.00028	187.91602
3s-9p	0.00000	187.91602

Experimental value of the total polarizability is 145.1±13.5.[21]

I-4. AUTOIONIZATION STATES OF THE e^--Li AND e^--Na SYSTEMS

A. Theory of the Autoionization States

In this section we summarize the theory of the compound atom or autoionization states, using the approach developed by Feshbach,[23] and applied to atomic systems by several other authors.[24-26]

Consider an elastic scattering problem. Let $\vec{q}$ represent the coordinates of the incident particle relative to the heavy nucleus of the target atom and let $\vec{r}$ represent the coordinates of the atomic electrons. The total Hamiltonian and total energy of the system, target atom plus incident particle, are denoted by H and E, respectively. The ground state of the target has a wave function $\psi_o(\vec{r})$ and an energy E_o. $E'=E-E_o$ is then the incident particle energy. The excited state wave functions and energies of the target are denoted by $\psi_1(\vec{r})$, $\psi_2(\vec{r})\cdots$, and E_1, $E_2,\cdots$, respectively. By assumption, E lies below E_1, or equivalently E' is smaller than E_1-E_o, so that excitation is not energetically possible.

The regular solution of $\Psi_L(\vec{r},\vec{q})$ of

$$(H-E)\ \Psi_L(\vec{r},\vec{q}) = 0 \qquad (44)$$

which satisfies the boundary condition that as $q\to\infty$,

$$\Psi_L(\vec{r},\vec{q}) \rightarrow \psi_o(\vec{r})\ P_L(\cos\theta)\ \sin(kq - \tfrac{1}{2}L\pi+\eta_L)/q\ , \qquad (45)$$

determines the phase shift η_L to within a multiple of π. θ is the angle between $\vec{q}$ and some fixed axis.

Following Feshbach[23] and Hahn, O'Malley and Spruch,[24] we now introduce a pair of projection operators, P and Q, which operate in the space of the target particle coordinates. P is defined by

$$P = |\psi_o\rangle\langle\psi_o|\ , \qquad (46)$$

that is, P projects onto the ground state of the target, while Q projects onto all of the excited states of the target, including the continuum states. Therefore, we have

$$P + Q = 1\ . \qquad (47)$$

We can rewrite Eq. (44) as

$$(P+Q)\ (H-E)\ (p+Q)\Psi_L = 0\ . \qquad (48)$$

Since P and Q operate in orthogonal space, Eq. (48) can be rewritten into a pair of equations

$$P(H-E)\ (P+Q)\Psi_L = 0\ , \qquad (49)$$

$$Q(H-E)\ (P+Q)\Psi_L = 0. \tag{50}$$

Ψ_L can be rewritten in the form

$$\Psi_L(\vec{r},\vec{q}) = \sum_i \psi_i(\vec{r})\ u_i(\vec{q})\ , \tag{51}$$

where, as $q\to\infty$,

$$u_o(\vec{q}) \to [\sin(kq - \tfrac{1}{2}L\pi+\eta_L)/q]\ P_L(\cos\theta)\ , \tag{52}$$

and where, for $i\neq 0$, $u_i(q)$ vanishes more rapidly than $1/q$. We then have

$$Q\Psi_L = \sum_i{}' \psi_i(\vec{r})\ u_i(\vec{q})\ , \tag{53}$$

where the prime indicates that the sum is to be taken over the excited states only. It follows that $Q\Psi_L$ vanishes more rapidly than $1/q$ as $q\to\infty$. Now, for any Hermitian operator, Q, and function, ϕ, we have

$$\langle Q\phi|H|Q\phi\rangle = \langle\phi|QHQ|\phi\rangle\ , \tag{54}$$

QHQ may be considered as a single operator the eigenvalues of which have the continuum portion beginning not at E_o, as does that of H, but at E_1. QHQ <u>may</u> also have some discrete eigenvalues below E_1; if there exist N_L^Q

orthonormal states of total angular momentum L which satisfy

$$Q(H-E^Q_{Ln})\ Q\Phi^Q_{Ln} = 0\ , \quad n=1,2,\cdots N^Q_L\ , \tag{55}$$

with $E^Q_{Ln}<E_1$, the spectrum of $Q(H-E)Q$ in the space of total angular momentum L will include the N^Q_L discrete eigenvalues, $E^Q_{Ln}-E$, and the continuum bounded from below by the positive value of E_1-E. The discrete states are the autoionization states below the level E_1. If, for example, $E_2<E<E_3$, we redefine

$$P = \sum_{i=0}^{2} |\psi_i\rangle \langle\psi_i| \ , \tag{56}$$

and the autoionization states obtained will be those below the level of E_3. These states will appear just like ordinary bound states in the calculation.

To explain why the autoionization states are resonance states, it is convenient to use the properties of the coupled channel S-matrix.[27] We consider a finite number of channels with two particles in each. The coupled equations describing the radial motion of the scattering particles are:

$$\left(\frac{d^2}{dr^2} - \frac{\ell_i(\ell_i+1)}{r^2} + k_i^2\right)\ u_{ij}(r) = \sum_{k=1}^{N} V_{ik}(r)\ u_{kj}(r)\ ,$$

$$i=1,\cdots N, \quad j=1,\cdots N\ . \tag{57}$$

The channel energies k_i^2 are related to the total energy E of the system by

$$E = k_i^2 + \varepsilon_i \ , \quad i=1,\cdots N \tag{58}$$

where ε_i are the sum of the internal energies of the two colliding particles in channel i. ℓ_i are the channel momenta.

We can find, in general, N independent solutions of Eq. (57) regular at the origin. The S-matrix is defined in terms of these by

$$u_{ij}(0) = 0 \ ,$$

$$u_{ij}(r) \underset{r\to\infty}{\sim} k_i^{-\frac{1}{2}} \{\exp[-i(k_i r - \tfrac{1}{2}\ell_i\pi)]\delta_{ij} - \exp[i(k_i r - \tfrac{1}{2}\ell_i\pi)S_{ij}\}, \quad i=1,\cdots N, \ j=1,\cdots N \ . \tag{59}$$

S_{ij} is an NxN matrix, each element of which is a function of the N channel momenta $k_1,\cdots k_N$.

The value of S is uniquely given by k_1 if the sign ambiguities in the relations

$$k_2 = \pm(k_1^2+\varepsilon_1-\varepsilon_2)^{\frac{1}{2}},\cdots k_N = \pm(k_1^2+\varepsilon_1-\varepsilon_N), \tag{60}$$

are resolved. The signs can be chosen in 2^{N-1} different ways, and consequently the S-matrix can only be made single valued, or uniformized, by introducing 2^{N-1} sheets in the complex k_1 plane. There is no reason why the k_1 plane should be preferred to the E plane, and the uniformization of S is usually carried out by introducing 2^N sheets in the E plane.

We show in Fig. 1-a an example of the cut E plane, where all the branch cuts are chosen to run from $k_i=0$ along the real axis to $E=+\infty$. The physical scattering region is along the upper rim of all the cuts. On the physical sheet, obtained by continuing from the physical region without crossing any branch cuts, all the k_i have positive imaginary parts. It follows that the wave function at a pole of S on the physical sheet is normalizable, and thus the poles on the physical sheet must be at a real energy lying below the lowest threshold. The circles in Fig. 1-a are bound states lying below the lowest threshold.

Consider now the example of two coupled channels illustrated in Figs. 1-b to 1-d. In the absence of coupling between the channels, the S-matrix is diagonal with poles both in $S_{11}(k_1)$ and in $S_{22}(k_2)$, as shown in Figs. 1-b and 1-c, respectively. B is a bound state in channel 1, and R_1 and R_3 are resonance states in channel 1

and 2, respectively, with or without the coupling potential V_{12}. But R_2, an apparent bound state in channel 2 without the coupling potential, is "forced off" the real axis when V_{12} is switched on and becomes a closed channel resonance state.

B. The Autoionization States of e^--Li and e^--Na Systems

In Sec. I-2, we expressed the orbitals of the "binding" electron in terms of the single particle orbitals obtained for the N-1 electron system, Eq. (33). It not only reduced the work of generating the virtual orbitals as needed by Weiss,[9] but made the construction of the projection operator particularly convenient. By excluding any lowest excited state from the sum, ϕ^ν is made automatically orthogonal to that state.

Approximations to autoionization states of the e^--alkali atom systems can be readily obtained in the formalism used here. The accuracy of the binding energy (relative to the energy of the excited valence state to which the additional electron binds) will be comparable to that obtained for the electron affinity. As described in Sec. I-2B, single configuration Hartree-Fock wave functions can be obtained for the low lying excited states of Li and Na. Eq. (10) can be used for the wave function of the autoionization state if the summation over γ and ν excludes the ground state orbitals and other excited valence orbitals of energy lower than that of interest.

In Figure 2 we show the Hartree-Fock spectrum of the low-lying states of Li with configurations $1s^2n\ell$. Autoionization states below the $1s^2 3s$ state, for example, can be obtained by excluding the orbitals 1s, 2s, 2p from the summation in Eq. (10). In this manner we have obtained several shallow autoionization states below the $1s^2 3s$ and $1s^2 3p$ levels. Elastic scattering calculations by Karule and Peterkop[28] in the strong coupling (2s-2p) approximation have detected no resonances below the 2p excitation threshold, in agreement with the present results. However, since they have not coupled higher excited states the resonances associated with the autoionization states obtained here were not included. Burke and Taylor[29] claim to have found resonance states below the $1s^2 2p$ level, but we are quite satisfied that our result is correct and that no closed channel resonances exist below the $1s^2 2p$ threshold. The experimental results for the elastic scattering of electrons from Li[30] are suggestive of the resonances near the $1s^2 3p$ threshold but the data are insufficient to be conclusive.

The same method has been used to search for autoionization states of the e^--Na system. We show in Figure 3 the only state found for this case but it is difficult to say whether this is due to weaker interactions, compared to the e^--Li case, or due to the smaller number of single particle states with large spatial extent that are

included in the mixing.

V. CONCLUSIONS

We have formulated an analytic multiconfiguration Hartree-Fock method of determining accurate values for the electron affinity of alkali atoms. The essential difference between this method and the superposition of configurations method of Weiss[9] is that we use the lowest lying excited states obtained for the N-1 electron system in place of Weiss' virtual excited states thus saving the extra work in generating these states. The accuracy of this simplified method is practically the same as the SOC method. Due to this modification the projection techniques used for the determination of the autoionization states for the e^--alkali system become also simplified, and the location of these states, relative to the atomic excited states, can be found with essentially the same degree of accuracy as the electron affinity calculations. The detection of these autoionization states depends on the widths of the levels and we have not attempted to determine values of these widths in this work.

PART II

ELASTIC SCATTERING OF POSITRON FROM HYDROGEN: AN OPTICAL POTENTIAL CALCULATION

II-1. INTRODUCTION

In the theoretical calculation of positron-atom scattering at low energies, the difficulty is well known to be one of complexity. That is, the problem one faces is to make suitable approximations to the solution of the complicated, but known, many-body Schroedinger equation so that good results may be obtained with reasonable effort. One important effect the approximation scheme must take into account is the distortion effect, or polarization effect which arises from the distortion experienced by the atomic electrons in the presence of the Coulomb field of the incident positron. The distortion or polarization of the target atom in turn produces a potential on the incident positron. Various attempts have been made to take account of this polarization phenomenon. The case of S-wave positron-hydrogen scattering provides a good test of these approaches since accurate results have been obtained by Schwartz[31] in an extensive many-parameter variational calculation.

One class of approximations is non-variational in nature. This includes the adiabatic polarized orbital method[32] and the non-adiabatic extended polarization potential method of Callaway et al.[33] The former method[32] tends to overestimate the S-wave phase shifts while the latter method[33] tends to underestimate them. Because

these non-variational approaches do not yield a stationary property of the phase shifts, attention has recently shifted to variational methods, some of which yield bounds.[31,34,35]

The many-parameter variational approaches of Schwartz,[31] Hahn and Spruch,[36] and Burke and Taylor,[35] are capable of yielding reliable results. However, extension to more complicated atoms is very difficult. The close-coupling formalism,[16,37,38] in which the first few lowest lying states of hydrogen are included, yields poor results, mainly because of the neglect of excitation to the electron continuum which is of great importance in the hydrogen case.

This undesirable feature is partially eliminated by a modification of the close-coupling formalism which introduces localized pseudo states of the atom that effectively represent the continuum.[39-42] In considering the positron-hydrogen problem, Perkins[41] has coupled pseudo p and d states to the 1s state of hydrogen. Two adjustable parameters are used to maximize the lower-bound phase shifts. Burke et al[42] have close-coupled pseudo p and d states along with the 1s, 2s, and 2p states of hydrogen in a calculation of electron-hydrogen scattering. The pseudo states used yield the exact values of the polarizabilities $\alpha(1s\rightarrow p\rightarrow 1s)$, $\alpha(1s\rightarrow d\rightarrow 1s)$ and contain no

adjustable parameters.

One of the most fruitful approaches to the low-energy scattering of positron from hydrogen has been formulated by Drachman[43] using the lower-bound principle of Gailitis.[44] The Hilbert space of the atom is decomposed into the ground state and the first order perturbed atomic state which implicitly includes all atomic states. This method has been extended to the electron-hydrogen elastic scattering problem by Oberoi and Callaway.[45]

Another general approach is the optical potential method, where the effect of the target atom on the scattering particle is represented by an equivalent one-body potential. The optical potential was first applied to atomic scattering problems by Mittleman and Watson.[46] A formal expansion for the optical potential was derived by Bell and Squires.[47] They have showed that the optical potential may be expressed as a many-body perturbation expansion developed by Brueckner[48] and Goldstone[49] and individual terms in the expansion can be represented by diagrams. The advantage of using many-body perturbation theory over the more conventional approaches mentioned above is that many-body perturbation theory starts from first principles and gives a well defined procedure for improving upon a given approximate calculation. The method has been applied by Pu and Chang[50] to the problem

of electron-helium scattering and by Kelly[51] to the problem of triplet scattering of S-wave electrons from hydrogen. The main difficulty of this approach is that the numerical work involved in the calculation is lengthy. However, extension to more complicated systems is straightforward. First order and second order diagrams can be readily and accurately evaluated, but higher order diagrams can only be approximated in practice. For this reason it is desirable to formulate the problem in such a manner as to minimize these higher order effects.

The objectives of the present calculation include the extension of the many-body formalism to the problem of the elastic scattering of positrons from atoms and the consideration of various possible choices of the single particle potential. In Sec. II-2 we give the extension of the formalism to the problem of positron-atom scattering. Sec. II-3 contains a discussion of the choices of the single particle potential of the positron and in Sec. II-4 we present the results. Conclusions are contained in Sec. II-5.

II-2. FORMALISM

The application of the formal optical potential of Bell and Squires[47] to the scattering of electrons from atoms has been made by Pu and Chang[50] and Kelly.[51] We briefly discuss the extension of this formalism to the scattering of positrons from atoms.

The total Hamiltonian describing an incident positron and an atom of Z electrons is given by

$$H(A,x) = H_A(A) + T_+(x) - \sum_{i=1}^{Z} v(ix), \tag{61}$$

where H_A is the atom Hamiltonian

$$H_A(A) = \sum_{i=1}^{Z} T(i) + \sum_{i>j}^{Z}\sum v(ij). \tag{62}$$

T(i) is the sum of the kinetic energy and the nuclear potential energy of the i^{th} electron, T_+ is the corresponding quantity for the positron, and the two-body interactions are given by

$$v(ij) = e^2/|\vec{r}_i-\vec{r}_j|,$$

$$v(ix) = e^2/|\vec{r}_i-\vec{x}|. \tag{63}$$

The scattering equation of interest is

$$H(A,x)\ \Psi(A,x) = (E_A+\varepsilon)\ \Psi(A,x), \tag{64}$$

where E_A is the total energy of the ground state of the atom and ε is the energy of the incident positron. The optical potential formalism, described below, replaces this many-particle Schroedinger equation with a single-particle equation,

$$(h(x) + V_{op})\psi(x) = \varepsilon\psi(x), \tag{65}$$

the solution of which yields the exact scattering phase shifts. Here h is a zero-order positron Hamiltonian and V_{op} is the optical potential which are obtained as follows.

The interaction between the particles can be approximated by single-particle electron and positron potentials, V and V_+ respectively. We then define the zero-order Hamiltonians

$$h(x) = T_+(x) + V_+(x), \tag{66a}$$

$$H_A^{(0)}(A) = \sum_{i=1}^{Z} (T(i) + V(i)), \tag{66b}$$

$$H^{(0)}(A,x) = h(x) + H_A^{(0)}(A), \tag{66c}$$

from which one obtains the many-body perturbation

$$H'(A,x) = H(A,x) - H^{(0)}(A,x),$$

$$= \sum_{i>j}^{Z} \sum v(ij) - \sum_{i=1}^{Z} v(ix) - \sum_{i=1}^{Z} V(i) - V_+(x).$$

(67)

The only restriction placed on the single-particle potentials is that they be Hermitian so that the single-particle wave functions

$$(T(i)+V(i))\phi_n(i) = \varepsilon_n \phi_n(i), \tag{68a}$$

$$(T_+(x)+V_+(x))\phi_K(x) = \varepsilon_K \phi_K(x), \tag{68b}$$

form an orthonormal set.[14,52]

The zero-order atomic wave function, $\Phi_0^{(0)}(A)$, is chosen to be a Slater determinant formed from Z single-particle states ϕ_n representing the ground state of the atom. We refer to these states as the unexcited states.

Continuum solutions of the single-particle equations, Eqs. (68), are normalized as follows

$$\phi = r^{-1} R(r) Y_{\ell m}(\theta,\phi) \chi_{m_s},$$

$$R(r) \underset{r\to\infty}{\to} \cos(kr + \delta_\ell - \tfrac{1}{2}(\ell+1)\pi) . \tag{69}$$

With this normalization the summation over continuum states is replaced by $(2/\pi)\int_0^\infty dk$.[18,22] In this calculation bound states are summed up to principal quantum number N=10. Higher states are included using the estimation formula of Kelly.[22,53]

The optical potential as obtained by Bell and Squires[47] is

$$V_{op} = \langle \Phi_0^{(0)} | \sum_{\substack{m=0 \\ LP}}^{\infty} H' \left(\frac{H'}{E_A^{(0)} + \varepsilon_{K_o} - H^{(0)} + i\delta} \right)^m | \Phi_0^{(0)} \rangle . \quad (70)$$

This sum can be represented by a series of diagrams. The notation, LP, refers to the fact that only those terms which are linked and proper (as specified by Bell and Squires[47]) are to be retained. The rules for evaluating diagrams need only minor modifications from those used when all the particles are identical.[22,53] One must distinguish positron lines from electron lines. We use a double bar to indicate a positron. The single-particle interactions are different depending upon whether they are attached to a positron line (V_+) or an electron line (V). Finally, each two-body electron-positron interaction introduces an additional minus sign to the overall sign of the diagram.

Rather than attempt to solve the scattering equation, Eq. (65), with the complicated non-local potential, Eq.

(70), or the equivalent radial equation

$$(L-\varepsilon_{K_o})R_{K_o} = (-\frac{d^2}{dr^2} + \frac{2Z}{r} + \frac{\ell(\ell+1)}{r^2}$$

$$+ V_+ + V_{op} - \varepsilon_{K_o})R_{K_o} = 0, \qquad (71)$$

we use the variational principle of Hulthen[54] which yields a stationary property for the phase shift although it does not give a bound. Constructing a trial potential, V_t, and its scattering solution

$$(L_t-\varepsilon_{K_o})R^t_{K_o} = (-\frac{d^2}{dr^2} + \frac{2Z}{r} + \frac{\ell(\ell+1)}{r^2}$$

$$+ V_t - \varepsilon_{K_o})R^t_{K_o} = 0, \qquad (72)$$

we obtain the variational estimate of the phase shift

$$\delta = \delta_t - \langle R^t_{K_o}|L-\varepsilon_{K_o}|R^t_{K_o}\rangle/K_o$$

$$= \delta_t - \langle R^t_{K_o}|L-L_t|R^t_{K_o}\rangle/K_o$$

$$= \delta_t - \langle R^t_{K_o}|V_+ + V_{op} - V_t|R^t_{K_o}\rangle/K_o . \qquad (73)$$

The normalization, Eq. (69), is assumed. One can use different forms for the potentials V_+ and V_t, but since the motivation for choosing each of these potentials is

the same we identify V_t with V_+. The result is then

$$\delta = \delta_t - \langle K_o | V_{op} | K_o \rangle / K_o \ . \tag{74}$$

In the following section we discuss various possible choices for the single-particle potential, V_+.

II-3. THE CHOICE OF THE SINGLE PARTICLE POTENTIALS

The positron-atom problem has a computational advantage over the associated electron-atom problem in that exchange diagrams involving the scattered particle do not occur because the Pauli principle does not enter. A serious disadvantage is that correlation effects are generally larger for the positron than for the electron. Therefore one must judiciously choose the positron single-particle potential to include as much as possible of the correlation effects and minimize the higher-order correlations. In particular, it is desirable to choose V_+ such that it includes the screening effect of all the atomic electrons and also includes a model potential which approximates the polarization effects. The electron single-particle potential, V, should be chosen to represent the screening of Z-1 electrons (generally the lowest lying electrons). Such a choice gives rise to both bound and continuum excited electron states. Pu and Chang[50] and Kelly[51] chose a single-particle electron potential which did not give rise to bound excited states. Kelly[51] then found that second-order effects accounted for about 70% of the full correlation effect in triplet S-wave electron-hydrogen scattering and about 60% of the dipole polarizability. By estimating higher-order effects he was able to obtain good agreement with the exact results.

For the application considered here, the scattering of S-wave positron from hydrogen, we choose V=0. The excited electron states, ϕ_k, are just the hydrogenic functions. Diagrams which then arise, through third order, are shown in Figure 4. Only the two terms of H' in Eq. (67) which contain positron operators will contribute. The perturbation expansion of the matrix element gives the following terms through third order

$$-\langle K_o|V_+|K_o\rangle, \tag{75a}$$

$$-\langle K_o n|v|K_o n\rangle = \langle K_o|V_H|K_o\rangle, \tag{75b}$$

$$\sum_{Kk} \frac{\langle K_o n|v|Kk\rangle\langle Kk|v|K_o n\rangle}{\varepsilon_n+\varepsilon_{K_o}-\varepsilon_k-\varepsilon_K}, \tag{75c}$$

$$-\sum_{\substack{KK'\\kk'}} \frac{\langle K_o n|v|K'k'\rangle\langle K'k'|v|Kk\rangle\langle Kk|v|K_o n\rangle}{(\varepsilon_n+\varepsilon_{K_o}-\varepsilon_{K'}-\varepsilon_{k'})(\varepsilon_n+\varepsilon_{K_o}-\varepsilon_K-\varepsilon_k)}, \tag{75d}$$

$$-\sum_{KK'k} \frac{\langle K_o n|v|K'k\rangle\langle K'|V_+|K\rangle\langle Kk|v|K_o n\rangle}{(\varepsilon_n+\varepsilon_{K_o}-\varepsilon_{K'}-\varepsilon_k)(\varepsilon_n+\varepsilon_{K_o}-\varepsilon_K-\varepsilon_k)}. \tag{75e}$$

Here we denote the hydrogenic 1s state by n and V_H is the (attractive) Hartree potential

$$V_H = -\langle n|v|n\rangle. \tag{76}$$

The standard choice of V_+ is such as to make the first-order corrections, Eq. (75a) plus Eq. (75b), vanish. However, the second-order correlation effect, Eq. (75c), is large in this case and we choose V_+ in such a manner as to partially compensate for this polarization effect. Preliminary calculations including first- and second-order diagrams with intermediate states restricted to the multipoles $\ell \leq 3$ were performed using four choices of V_+: (i) $V_+=V_H$, (ii) $V_+=V_H+V(\text{Bethe})$ where V(Bethe) is the adiabatic dipole polarization potential,[55] (iii) $V_+=V_H+V(\text{Bethe})+V(\text{Reeh})$ where V(Reeh) is the adiabatic quadrupole polarization potential,[56] (iv) $V_+=V_H+V(\text{Buckingham})$ where

$$V(\text{Buckingham}) = -4.5/(r^2+\Delta^2)^2 \qquad (77)$$

and Δ is used as an adjustable parameter.[57] A value of $\Delta \approx 1.85$ was found to maximize the second-order results.

Choices (ii), (iii), and (iv) (with $\Delta=1.85$) were found to give essentially the same second-order phase shifts, with $V_+=V_H+V(\text{Bethe})$ giving slightly larger values. However, choosing $V_+=V_H$ gives decidedly inferior results at low energies. This is illustrated in Figure 5 where we plot $\delta_t(\text{Hartree})$, $\delta_t(\text{Hartree+Bethe})$, $\delta(\text{Hartree})$, $\delta(\text{Hartree+Bethe})$ and Schwartz's[31] values for δ. The agreement of the second-order phase shifts for all model potentials at the high energy portion of the spectrum

infers that the variational method of computing the phase shifts should be quite good away from threshold. The results discussed in the following section were computed using the choice $V_+=V_H+V(\text{Bethe})$. However, we shall refer to the difference between the Schwartz result and the Hartree result as the full correlation correction to the phase shift. The zero energy scattering solution to Eq. (68b) was found to have no zeros other than at the origin and therefore there exists no bound states of the zero-order positron Hamiltonian, h.

II-4. RESULTS

With the choice $V_+=V_H+V(\text{Bethe})$ the first-order contribution becomes

$$\langle K_o|V_{op}^{(1)}|K_o = -\langle K_o|V(\text{Bethe})|K_o\rangle, \tag{78}$$

which is the sum of Eq. (75a) and Eq. (75b). This partially cancels the second-order matrix element Eq. (75e). In Table IX we list the various contributions to δ through second order. These results are subdivided into the multipole of the intermediate states, and further subdivided into contributions from bound excited states k(b) and from continuum excited states k(c). Bound f states are not included since their contribution is small. We estimate that an error of about 1% of the difference between the static results and the exact results is made when one neglects multipoles $\ell\geq 4$ in second order. The second-order phase shifts are also plotted in Figure 4. One observes that approximately 67%-80% of the total correlation effect is accounted for in second order. This is to be compared with the results of Hahn and Spruch[36] who obtain 85%-89% of the full correlation effect using multipoles $\ell\leq 3$ and including all orders of interactions.

The radial integrals were performed using $R_{max}=45$. The trial phase shift, δ_t, and the first-order matrix

element, Eq. (78), were extended to infinity using the technique of Levy and Keller.[58] A check on the numerical accuracy of the second-order p and d multipole contributions was made by simultaneously computing the adiabatic matrix elements which are obtained by setting ε_K equal to ε_{K_o} in the denominator of Eq. (75c). The results were compared to the matrix elements of the Bethe potential and the Reeh potential and were found to agree to approximately .5%. The latter figure then serves as our estimate of the numerical accuracy of the second-order results.

Higher order correlations involving multipoles $\ell \leq 3$ are estimated using the third-order diagrams according to the techniques devised by Kelly.[51,53] The most important intermediate electron states of the second-order matrix element are 2s, 2p, ks$\tilde{}$.5s, kp$\tilde{}$.5p, kd$\tilde{}$.75d and kf$\tilde{}$1.0f. Similarly we find that the most important intermediate positron states are given by Ks$\tilde{}$.75s, Kp$\tilde{}$(.25+.8K_o)p, Kd$\tilde{}$(.75+.6K_o)d and Kf$\tilde{}$(1.25+.6K_o)f.

For a particular ℓ value of the excited states K, k in Fig. 4c, with K, k chosen to be the typical excitations of importance just given, the ratios

$$t(K,k) = -\sum_{K'k'} \frac{\langle K_o n|v|K'k'\rangle\langle K'k'|v|Kk\rangle}{\varepsilon_n+\varepsilon_{K_o}-\varepsilon_{K'}-\varepsilon_{k'}} / \langle K_o n|v|Kk\rangle , \tag{79}$$

$$a(K,k) = -\sum_{K'} \frac{\langle K_o n|v|K'k\rangle\langle K'|V_+|K\rangle}{\varepsilon_n+\varepsilon_{K_o}-\varepsilon_{K'}-\varepsilon_k} / \langle K_o n|v|Kk\rangle \qquad (80)$$

are constructed. The motivation for forming these ratios becomes clear when one compares the third-order matrix elements, Eq. (75d) and Eq. (75e), with the second-order matrix element, Eq. (75c). The ratio t has been found by Kelly[51,53] to be reasonably accurate approximation for the ratio of the ladder diagram, Fig. 4d to the second-order diagram, Fig. 4c. Similarly, a approximates the ratio of Fig. 4e to Fig. 4c.

In order to facilitate the discussion we subdivide the contributions to the ladder approximation, t(K,k), into its diagonal part and its non-diagonal parts. For a given k the diagonal parts considered, $t_D(k)$ are as follows:

$$\begin{aligned}
&k = 2s \to k' = 2s,\\
&k = ks \to k' = \text{continuum } s,\\
&k = 2p \to k' = 2p,\\
&k = kp \to k' = \text{continuum } p,\\
&k = kd \to k' = \text{continuum } d,
\end{aligned} \qquad (81)$$

while the non-diagonal parts considered, $t_{ND}(k\to k')$, are

$$k = 2s \rightarrow k' = \text{all } s \ (\neq 2s),$$
$$k = ks \rightarrow k' = \text{bound } s,$$
$$k = 2p \rightarrow k' = \text{all } s, \text{ all } p \ (\neq 2p), \text{ all } d, \text{ all } f,$$
$$k = kp \rightarrow k' = \text{all } s, \text{ bound } p, \text{ all } d, \text{ all } f,$$
$$k = kd \rightarrow k' = \text{bound } d. \qquad (82)$$

We have not considered diagonal third-order corrections for intermediate f and bound d states since their contribution is small. Similarly, some (presumably small) non-diagonal third-order effects have not been included.

In evaluating Eq. (80) the intermediate matrix element, $\langle K'|V_+|K\rangle$, diverges for K'=K if we let R_{max} approach infinity.[53] However, the integration over K' removes this infinity. A similar phenomenon occurs for $t_D(k)$. Further, there is substantial cancellation between $t_D(k)$ and $a(k)$. The third-order ratios have been computed for the energies of interest. In Table X we list the results for the single case $K_o=.3$.

Higher-order corrections are estimated in the following manner. Diagonal ladder diagrams can be summed to all orders since the ratio of the (n+1)st-order diagram to the n^{th}-order diagram is approximately given by $t_D(k)+a(k)$. The net effect is to modify the second-order diagram associated with the state k by the factor

$$(1-t_D(k)-a(k))^{-1} . \qquad (83)$$

Non-diagonal third-order diagrams contribute a factor

$$(1-t_D(k)-a(k))^{-1}\ t_{ND}(k\to k')(1-t_D(k')-a(k'))^{-1}\ . \qquad (84)$$

The transitions considered are given in Eq. (82). A factor of 2 should be included for the ℓ changing third-order non-diagonal diagrams to account for both $k\to k'$ and $k'\to k$. We also estimate some small fourth-order diagrams of the type $k\to k'\to k$ which give rise to a factor

$$(1-t_D(k)-a(k))^{-1}\ t^2_{ND}(k\to k')(1-t_D(k)-a(k))^{-1}\ . \qquad (85)$$

Using these estimates we compute a "coefficient of enhancement", Ce, for each of the second-order contributions listed in Table IX. We have set Ce=1 for bound d and continuum f contributions. The Ce value for s and d states includes only the ℓ non-changing transitions as indicated in Eq. (82). The ℓ changing corrections have been included in the p state Ce value. These results are listed in Table XI.

The final value of the phase shift is then obtained from

$$\delta = \delta_t - [\langle K_o|V^{(1)}_{op}|K_o\rangle + \sum_i Ce(i)\langle K_o|V^{(2)}_{OP}(i)|K_o\rangle]/K_o\ , \qquad (86)$$

where the summation runs over those contributions to the second-order optical potential listed in Table IX. Table XII contains the results of our calculation and compares them with the variational calculation of Hahn and Spruch.[36] The Hahn and Spruch results include multipoles $\ell \leq 3$ and constitute an accurate estimate of the best results one can obtain with just these multipoles.

The present calculation, which includes only intermediate s, p, d and f states contains about 8% less of the full correlation effect than the corresponding calculation of Hahn and Spruch. Subsidiary calculations were performed in which only s, p, d and only s, p states were included. The difference with the corresponding calculations of Hahn and Spruch were 4% and 1% respectively. The good agreement of the results when only s, p states are included suggests that the variational approximation used here, Eq. (73), is sufficient if the single-particle potential is properly chosen. We believe the growing discrepancy with increasing multipoles is partly due to the techniques used for estimating the higher-order effects and partly due to the total neglect of fourth-order diagrams of the type $s \to p \to d$, $p \to d \to f$, and $p \to p' \to s,d$ where the first transition is non-diagonal.

II-5. SUMMARY AND CONCLUSIONS

We have calculated phase shifts for the S-wave scattering of positrons from hydrogen using a many-body optical potential. A single-particle positron potential has been chosen which effectively minimizes third- and higher-order correlations. These higher-order effects are still large and present techniques seriously underestimate their contribution. In the model problem where only s, p, d intermediate states are allowed to enter, the present formulation agrees to within 5% of the "exact" answer.[36] This is consistent with the results of the triplet S-wave electron-hydrogen scattering calculation of Kelly[51] where only these multipoles are important.

The contribution from multipoles $\ell \geq 3$ is known to be large.[36] Second-order contributions from these multipoles have been found to be small in this calculation. Attempts to estimate their contribution in third- and higher-orders give substantially smaller corrections than can be inferred from the calculation of Hahn and Spruch.[36] For this reason we have not attempted to include multipoles $\ell \geq 4$.

The optical potential calculation of Drachman[43] in which all multipoles are included in a non-adiabatic manner gives excellent results for the positron-hydrogen problem. However, extension of this formalism to the positron-helium problem necessitated an approximation and the results

are somewhat poorer. We expected that an application of the present many-body formalism to the positron-helium problem would give better results than those obtained here for the positron-hydrogen case, because the substantially smaller polarizability of helium should give smaller higher-order correlations and smaller errors in estimating them. However, after making a few calculations to the second-order for the positron-helium case, we found that the improvement over the positron-hydrogen case was negligible, and the work on the positron-helium problem was discontinued.

TABLE IX: CONTRIBUTIONS TO THE SECOND-ORDER S-WAVE PHASE SHIFT (IN RADIANS) FOR POSITRON-HYDROGEN SCATTERING USING THE SINGLE-PARTICLE POSITRON POTENTIAL $V_+ = V_{Hartree} + V_{Bethe}$. THE ℓ VALUE IS THE MULTIPOLE OF THE BOUND (b) OR CONTINUUM (c) EXCITED ELECTRON STATES.

K_o	0.0[a]	0.1	0.2	0.3
δ_t	-1.4587	.0982	.1139	.0870
$V_{op}^{(1)}$	2.7803	-.2094	-.2836	-.2964
$V_{op}^{(2)}$ ($k\ell$=c0)	- .0544	.0048	.0080	.0104
$V_{op}^{(2)}$ ($k\ell$=b0)	- .0950	.0083	.0139	.0179
$V_{op}^{(2)}$ ($k\ell$=c1)	- .6956	.0545	.0785	.0871
$V_{op}^{(2)}$ ($k\ell$=b1)	-1.4705	.1038	.1283	.1230
$V_{op}^{(2)}$ ($k\ell$=c2)	- .1877	.0158	.0233	.0255
$V_{op}^{(2)}$ ($k\ell$=b2)	- .0250	.0020	.0025	.0022
$V_{op}^{(2)}$ ($k\ell$=c3)	- .0494	.0042	.0062	.0068
$\delta^{(2)}$	-1.2561	.0822	.0910	.0635

a) The K_o=0 entries are contributions to the scattering length.

TABLE IX: (CONTINUED)

K_o	0.4	0.5	0.6	0.7
δ_t	.0415	-.0102	-.0622	-.1115
$v_{op}^{(1)}$	-.2868	-.2697	-.2509	-.2327
$v_{op}^{(2)}$ (kℓ=c0)	.0125	.0147	.0171	.0198
$v_{op}^{(2)}$ (kℓ=b0)	.0214	.0250	.0291	.0345
$v_{op}^{(2)}$ (kℓ=c1)	.0890	.0883	.0860	.0826
$v_{op}^{(2)}$ (kℓ=b1)	.1106	.0953	.0814	.0705
$v_{op}^{(2)}$ (kℓ=c2)	.0251	.0235	.0214	.0191
$v_{op}^{(2)}$ (kℓ=b2)	.0018	.0013	.0010	.0007
$v_{op}^{(2)}$ (kℓ=c3)	.0066	.0060	.0053	.0046
$\delta^{(2)}$	.0218	-.0258	-.0719	-.1123

TABLE X: THIRD-ORDER RATIOS FOR K_o=.3

$t_D(2s)+a(2s)$	-.5487
$t_D(ks)+a(ks)$	-.2808
$t_D(2p)+a(2p)$	-.0478
$t_D(kp)+a(kp)$	-.0017
$t_D(kd)+a(kd)$	.0627
$t_{ND}(2s \rightarrow s)$	.1188
$t_{ND}(ks \rightarrow s)$	.1461
$t_{ND}(2p \rightarrow s)$	-.0398
$t_{ND}(2p \rightarrow p)$	.0818
$t_{ND}(2p \rightarrow d)$	.0660
$t_{ND}(2p \rightarrow f)$	.0184
$t_{ND}(kp \rightarrow s)$	.0053
$t_{ND}(kp \rightarrow p)$	.0742
$t_{ND}(kp \rightarrow d)$	.0343
$t_{ND}(kp \rightarrow f)$	.0054
$t_{ND}(kd \rightarrow d)$	.0139

TABLE XI: Ce VALUES

K_o	Ce(b0)	Ce(c0)	Ce(b1)	Ce(c1)	Ce(c2)
0.0	.7262	.8735	1.1260	.9956	1.0646
.1	.7265	.8733	1.1521	1.0646	1.0754
.2	.7216	.8713	1.1649	1.1181	1.0811
.3	.7115	.8675	1.1644	1.1561	1.0817
.4	.6968	.8620	1.1475	1.1755	1.0755
.5	.6758	.8544	1.1237	1.1859	1.0679
.6	.6425	.8442	1.1031	1.1963	1.0627
.7	.5989	.8316	1.0822	1.2036	1.0585

TABLE XII: POSITRON-HYDROGEN PHASE SHIFTS IN RADIANS

K_o	Hartree	This Calculation[b]	Hahn and Spruch[b]	Schwartz
0.0[a]	.5822	-1.4091		-2.10
.1	-.0580	.0996		.151
.2	-.1145	.1187	.142	.188
.3	-.1682	.0938		.168
.4	-.2181	.0488	.076	.120
.5	-.2635	- .0043		.062
.6	-.3042	- .0540	-.029	.007
.7	-.3400	- .1038		-.054

a) The K_o=0 entries are scattering lengths

b) Including multipoles $\ell \leq 3$

FIGURE CAPTIONS

Figure 1 Poles and branch cuts in the single channel and coupled channel S-matrix.

Figure 2 Hartree-Fock energy levels for Li and the multiconfiguration Hartree-Fock ground state and metastable excited states of Li^-.

Figure 3 Hartree-Fock energy levels for Na and the multiconfiguration Hartree-Fock ground state and metastable excited states of Na^-.

Figure 4 Contributing diagrams to $\langle K_o | V_{op} | K_o \rangle$ through third order.

Figure 5 S-wave positron-hydrogen phase shifts in radians. δ_s=Schwartz results, δ_t=zero-order results, $\delta^{(2)}$=second-order results. H=Hartree single-particle potential, H+B=Hartree plus Bethe single-particle potential.

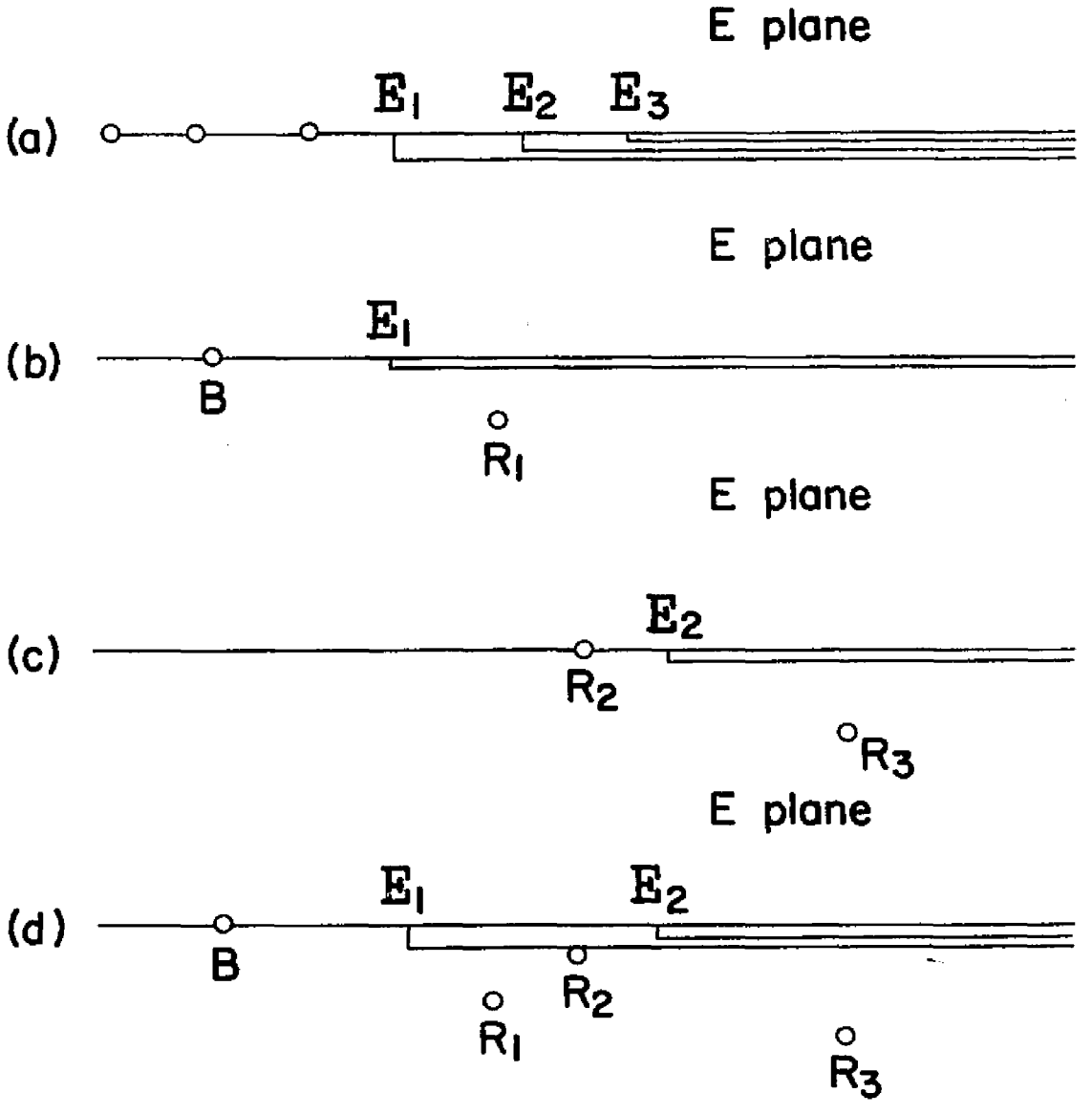

E plane
E1
E2
E3
(a)
E plane
E1
(b)
B
R1
E plane
E2
(c)
R2
R3
E plane
E1
E2
(d)
B
R2
R1
R3

Fig. 1

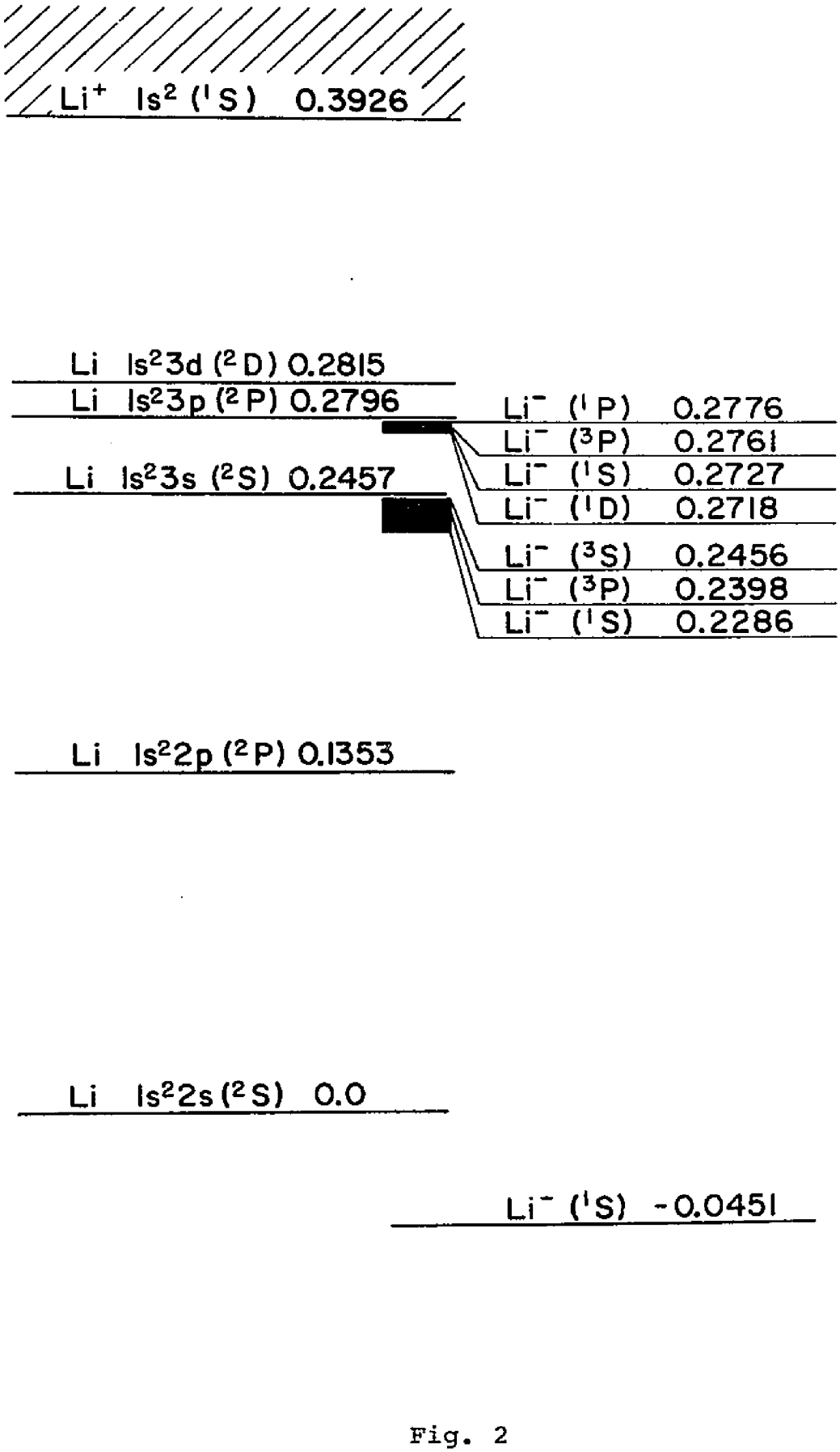
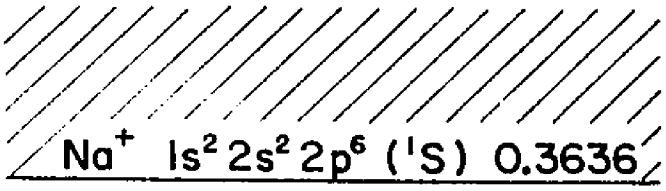

Li+ 1s2 (1S) 0.3926
Li 1s23d (2D) 0.2815
Li 1s23p (2P) 0.2796
Li 1s23s (2S) 0.2457
Li 1s22p (2P) 0.1353
Li 1s22s (2S) 0.0
Li- (1P) 0.2776
Li- (3P) 0.2761
Li- (1S) 0.2727
Li- (1D) 0.2718
Li- (3S) 0.2456
Li- (3P) 0.2398
Li- (1S) 0.2286
Li- (1S) -0.0451

Fig. 2



Na $1s^2 2s^2 2p^6 4p$ (^2P) 0.2632

Na $1s^2 2s^2 2p^6 3d$ (^2D) 0.2523

Na $1s^2 2s^2 2p^6 4s$ (^2S) 0.2235

Na^- (^1S) 0.2125

Na $1s^2 2s^2 2p^6 3p$ (^2P) 0.1453

Na $1s^2 2s^2 2p^6 3s$ (^2S) 0.0

Na^- (^1S) -0.0394

Fig. 3

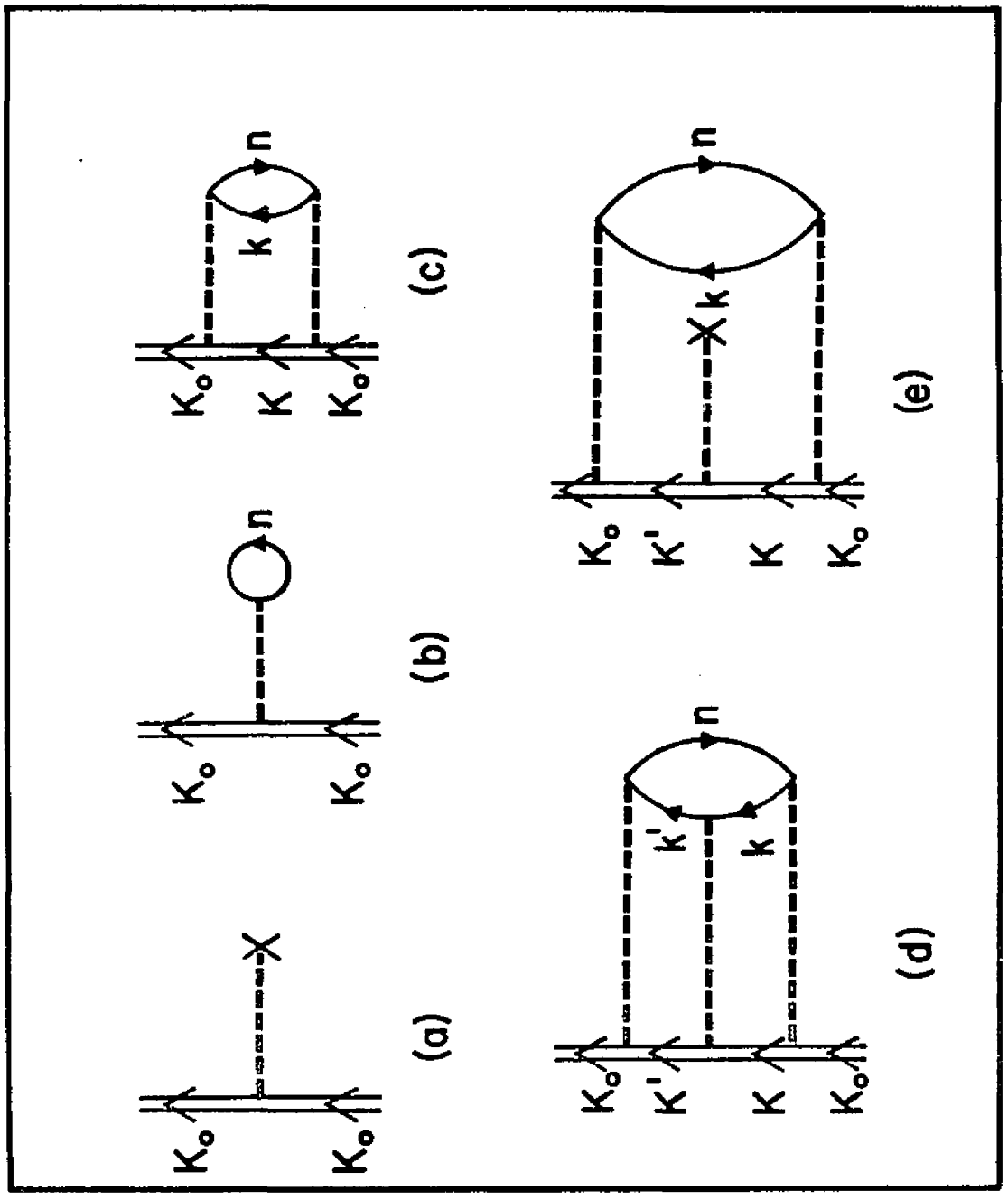


Fig. 4

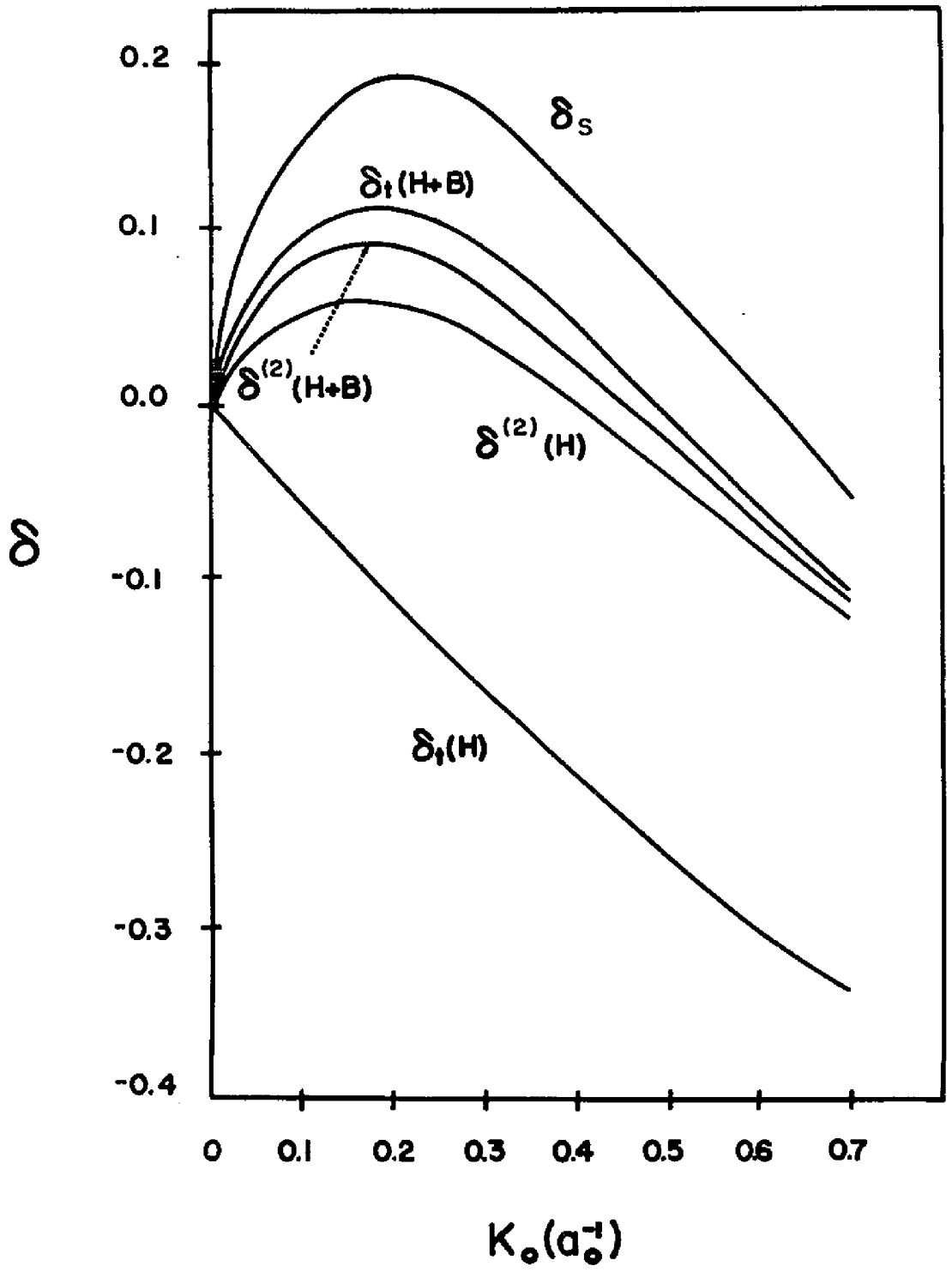

0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
δ
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
K₀(a₀⁻¹)
δs
δt(H+B)
δ(2)(H+B)
δ(2)(H)
δt(H)

Fig. 5

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APPENDIX I

This appendix demonstrates the method used to evaluate integrals which involve products of two determinantal wave functions.

Let

$$A = D_N(a_1 a_2 \cdots a_N), \tag{AI-1}$$

and

$$B = D_N(b_1 b_2 \cdots b_N), \tag{AI-2}$$

where D's are determinants of the form of Eq. (9) of the main text, and a_i, b_j belong to an orthonormal set of functions. In order that A and B are not identically zero, we must have

$$\langle a_i | a_j \rangle = \delta_{ij}\,, \tag{AI-3}$$

and

$$\langle b_i | b_j \rangle = \delta_{ij}\,. \tag{AI-4}$$

Let us also assume that A and B are permuted so that most elements are identical in pairs, $a_1=b_1, \cdots a_i=b_i, \cdots,$

except, maybe, $a_k \neq b_k$ and $a_t \neq b_t$.

We wish to evaluate

$$\langle A|F|B\rangle \tag{AI-5}$$

in which F are one- or two-particle operators. Let us expand A and B in a manner so that similar terms appear at corresponding locations in the expansion,

$$A = \frac{1}{\sqrt{N!}} \{a_1 a_2 \cdots a_N \pm \cdots \pm a_i a_j \cdots a_k \cdots a_t \cdots \pm a_i a_j \cdots$$

$$a_t \cdots a_k \cdots \pm \cdots\} ,$$

$$B = \frac{1}{\sqrt{N!}} \{b_1 b_2 \cdots b_N \pm \cdots \pm b_i b_j \cdots b_k \cdots b_t \cdots \pm b_i b_j \cdots$$

$$b_t \cdots b_k \cdots \pm \cdots\} .$$

(1) $F = 1$.

It is easy to see that $\langle A|B\rangle = 0$ unless A=B, since the general term of (AI-5) is

$$\frac{1}{N!} \langle a_i|b_j\rangle\langle a_k|a_\ell\rangle \cdots \langle a_y|b_z\rangle \tag{AI-6}$$

and is 0 unless the two elements in each pair are equal, or A=B. (We do not consider the case A=-B, since it is

trivial.)

For each term in A, the only non-vanishing product comes from a term in B which occupies the corresponding location as the term in A. There are a total of N! terms in the product, therefore,

$$\langle A|A\rangle = 1 . \qquad \text{(AI-7)}$$

(2) $F = \sum_{i}^{N} f(i)$, and B differs from A only in $a_t \neq b_t$.

The non-vanishing terms in the product must contain the factor $\langle a_t|f|b_t\rangle$, and each is equal to $\frac{1}{N!}\langle a_t|f|b_t\rangle$. Again, each term in A contributes one such term in the product, therefore,

$$\langle A|F|B\rangle = \langle a_t|f|b_t\rangle . \qquad \text{(AI-8)}$$

If A=B, then we may treat each a_i as a_t, thus

$$\langle A|F|A\rangle = \sum_{i}^{N} \langle a_i|f|a_i\rangle . \qquad \text{(AI-9)}$$

(3) $F = \sum_{i>j}^{N} g(i,j)$, and B differs from A only in $a_k \neq b_k$, $a_t \neq b_t$.

In this case, for each term in A, not only the corresponding term in B contributes, but also the term with k

and t exchanged, except that the latter product takes a (-) sign. Therefore,

$$\langle A|F|B\rangle = \langle a_k a_t|g|b_k b_t\rangle - \langle a_k a_t|g|b_t b_k\rangle . \qquad \text{(AI-10)}$$

If $a_k = b_k$, but $a_t \neq b_t$, we may treat each a_i, except a_t, as a_k,

$$\langle A|F|B\rangle = \sum_{i\neq t}^{N} [\langle a_i a_t|g|a_i b_t\rangle - \langle a_i a_t|g|b_t a_i\rangle]. \qquad \text{(AI-11)}$$

If A=B,

$$\langle A|F|A\rangle = \sum_{i>j}^{N}\sum^{N} [\langle a_i a_j|g|a_i a_j\rangle - \langle a_i a_j|g|a_j a_i\rangle], \qquad \text{(AI-12)}$$

These results were obtained by Condon and Shortley,[15] but the above presentation is quite different from theirs. To apply this method to our problem, we consider the following cases.

(4) F = 1, and B differs from A only in $a_N \neq b_N$ and they satisfy the conditions

$$\langle a_N|b_i\rangle = \langle b_N|a_i\rangle = 0 , \quad i=1,2,\cdots N-1 ,$$

but

$$\langle a_N|b_N\rangle \neq 0,1 .$$

The general term of $\langle A|B\rangle$, similar to Eq. (AI-6), is 0 unless a_i pairs with b_i, i=1,2,···N, and its value is $\frac{1}{N!}\langle a_N|b_N\rangle$. There are N! terms, therefore,

$$\langle A|B\rangle = \langle a_N|b_N\rangle \ . \qquad \text{(AI-13)}$$

(5) F = 1, and B differs from A in $a_{N-1}\neq b_{N-1}$, $a_N\neq b_N$, and they satisfy the conditions

$$\langle a_j|b_i\rangle = \langle a_i|b_j\rangle = 0 \ , \quad j=N-1,N; \quad i=1,2,\cdots N-2 \ ;$$

but

$$\langle a_j|b_{j'}\rangle \neq 0,1 \ , \quad j,j'=N-1,N \ .$$

There are two groups of non-vanishing terms in $\langle A|B\rangle$ now. One group contains terms similar to those of (4), that is, a_i pairs with b_i, i=1,2,···N, and each term is $\frac{1}{N!}\langle a_{N-1}|b_{N-1}\rangle\langle a_N|b_N\rangle$. The other group contains terms similar to the above but with b_N and b_{N-1} exchanged. Since there is one more exchange in one determinant than in the other, we need a (-) sign. Each term in the second group is $-\frac{1}{N!}\langle a_{N-1}|b_N\rangle\langle a_N|b_{N-1}\rangle$. Each group has N! terms, therefore,

$$\langle A|B\rangle = \langle a_N|b_N\rangle\langle a_{N-1}|b_{N-1}\rangle-\langle a_N|b_{N-1}\rangle\langle a_{N-1}|b_N\rangle. \qquad \text{(AI-14)}$$

(6) $F = \sum_i^N f(i)$, and A, B are determinants of (5).

The non-vanishing terms belong to the following groups.

(a) f goes with a_i and b_i, i=1,2,···N-2, and a_j pairs with b_j, j=N-1,N. The value of each term is

$$\frac{1}{N!} \sum_i^{N-2} \langle a_i|f|b_i\rangle \prod_{j\neq i}^{N-2} \langle a_j|b_j\rangle\langle a_{N-1}|b_{N-1}\rangle\langle a_N|b_N\rangle$$

$$= \frac{1}{N!} \langle a_{N-1}|b_{N-1}\rangle\langle a_N|b_N\rangle \sum_i^{N-2} \langle a_i|f|b_i\rangle .$$

(b) Same as (a) but b_N and b_{N-1} exchanged. The value of each term is

$$-\frac{1}{N!} \langle a_{N-1}|b_N\rangle\langle a_N|b_{N-1}\rangle \sum_i^{N-2} \langle a_i|f|b_i\rangle .$$

(c) f goes with a_{N-1} and b_{N-1}, and a_i pairs with b_i, i=1,···N-2. We have

$$\frac{1}{N!} \langle a_{N-1}|f|b_{N-1}\rangle\langle a_N|b_N\rangle .$$

(d) f goes with a_N and b_N, and a_i pairs with b_i, i=1,···N-2. We have

$$\frac{1}{N!} \langle a_{N-1}|b_{N-1}\rangle\langle a_N|f|b_N\rangle .$$

(e) Similar terms as in (c) and (d) but with b_N and b_{N-1} exchanged. Again we need a (-) sign, therefore,

$$- \frac{1}{N!} \{\langle a_{N-1}|f|b_N\rangle\langle a_N|b_{N-1}\rangle + \langle a_{N-1}|b_N\rangle\langle a_N|f|b_{N-1}\rangle\}.$$

The number of terms in each group is N!, therefore, $\langle A|F|B\rangle$ is the sum of the above multiplied by N!. The result is given in Eq. (15) of the main text.

(7) $F = \sum_{i>j}^{N} g(i,j)$, and A, B are determinants of (5).

The non-vanishing terms belong to the following groups.

(a) g goes with a_i, a_j and b_i, b_j, i,j=1,···N-2, and a_k pairs with b_k,k=N-1,N. Each term is

$$\frac{1}{N!} \sum_{i>j}^{N-2} \langle a_i a_j|g|b_i b_j\rangle\langle a_{N-1}|b_{N-1}\rangle\langle a_N|b_N\rangle.$$

(b) Same as (a) but b_i and b_j exchanged. The term value is

$$- \frac{1}{N!} \sum_{i>j}^{N-2} \langle a_i a_j|g|b_j b_i\rangle\langle a_{N-1}|b_{N-1}\rangle\langle a_N|b_N\rangle.$$

(c) g goes with a_i, a_{N-1} and b_i, b_{N-1}, i=1,···N-2, and a_j pairs with b_j, j=1,···N, but $j\neq i$ and $j\neq N-1$. The term value is

$$\frac{1}{N!} \sum_{i}^{N-2} \langle a_i a_{N-1} | g | b_i b_{N-1} \rangle \langle a_N | b_N \rangle .$$

(d) Same as (c) but b_i and b_{N-1} exchanged. The term is

$$- \frac{1}{N!} \sum_{i}^{N-2} \langle a_i a_{N-1} | g | b_{N-1} b_i \rangle \langle a_N | b_N \rangle .$$

(e) Same as (c) and (d) but exchange a_{N-1}, b_{N-1} with a_N, b_N. Since there are two more exchanges, the (-) sign is not needed. The sum of the two terms is

$$\frac{1}{N!} \sum_{i}^{N-2} \{ \langle a_i a_N | g | b_i b_N \rangle \langle a_{N-1} | b_{N-1} \rangle$$

$$- \langle a_i a_N | g | b_N b_i \rangle \langle a_{N-1} | b_{N-1} \rangle \} .$$

(f) g goes with a_{N-1}, a_N and b_{N-1}, b_N, and a_i pairs with b_i, i=1,...N-2. The term value is

$$\frac{1}{N!} \langle a_{N-1} a_N | g | b_{N-1} b_N \rangle .$$

(g) All of the above groups from (a) to (f) but with b_{N-1} and b_N exchanged. We, of course, need an extra (-) sign again.

The sum of all terms in the groups, (a) to (g), multiplied by N! gives the result of Eq. (16) of the main text.

VITA

Albert Ai-Chun Fung, son of Yu-Chin and Shih (Chang) Fung, was born in Tunghsien, Hopei, China, on September 16, 1917. He attended Yu-Ying Primary School and Peiping Practiced Middle School. He graduated in June 1935, and entered Peiping Normal University as a physics major. When the Sino-Japanese War broke in 1937, he transferred to Chiaotung University, Kweichow, China, and changed his major to Mining and Metallurgical Engineering. He received his Bachelor of Engineering degree in June 1941. He married Fefe, daughter of Jen-Jung and Wang Huang, on May 27, 1943. They have three daughters and a son. He was a Petroleum Engineer with Chinese Petroleum Corporation until January 1957, when he entered the Graduate School of Saint Louis University in physics, and received his Master of Science degree in January 1959, and became a member of The Society of The Sigma Xi in the same year. He was an Instructor in Physics at Whittier College, Whittier, California, from 1959 to 1967. In September 1967, he entered Louisiana State University on a teaching assistantship and is presently a candidate for the degree of Doctor of Philosophy in the Department of Physics and Astronomy.

EXAMINATION AND THESIS REPORT

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Major Field: Physics

Title of Thesis: Atomic Systems with a Closed Core Plus Two Electrons

Approved:

John J. Matese
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

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Date of Examination:

July 15, 1971